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The Wherry mine, Penzance, its history and its mineral productions.

(With Plates XXVI–XXVIII.)

By Sir Arthur Russell, Bart.

[Read March 9, 1939.]

IF the visitor standing at Wherry Town on the south-western end of the esplanade at Penzance looks seaward he will observe at low tide at some distance from the shore a low seaweed-clothed rocky shoal (fig. 1), and from his now very conventional surroundings it is difficult to realize that upon this shoal, always surrounded by water, there existed many years ago a rich tin mine, unique in the boldness of its conception, romantic in the extreme in its situation and execution, and withal the effort of a poor working miner.

Very fortunately in the year 1790, during the hey-day of its career, this remarkable mine was examined by a very competent observer in the person of John Hawkins (1761?–1841), F.R.S., of Trewithen, Cornwall, and Bignor Park, Sussex, and it is to him that we owe most of the details concerning its mode of working, &c.[1] The Wherry mine and its history have always fascinated me, as they must have many others, and in re-telling the old story I have endeavoured to collect all the known facts, both as to the mine itself, its mode of working, and its mineral productions, and in so doing pay tribute to its gallant and resourceful originator Thomas Curtis.

The low coast forming what was originally a part of the Western Green

[1] John Hawkins's account of the Wherry mine was published in four periodicals, two English, one French, and one German (see references at end). They are all substantially the same, that in the Annual Register being a little fuller; here he gives the date of his visit as 1790, whereas in Trans. Roy. Geol. Soc. Cornwall he gives it as 1791, the former being probably correct.

and now covered by Penzance esplanade and Wherry Town is composed of metamorphosed slaty rocks in part alternating with greenstone, these being well exposed at Lariggan Rocks a little to the west of the Wherry mine, where they contain much axinite in strings and lenticles. The foreshore has a sloping shingle beach through which rock projects at and below low-water mark. At a distance of about 240 yards from the coast and nearly parallel with it, the slate is traversed by an elvan or quartz-felspar-porphyry dike which has a south-westerly direction

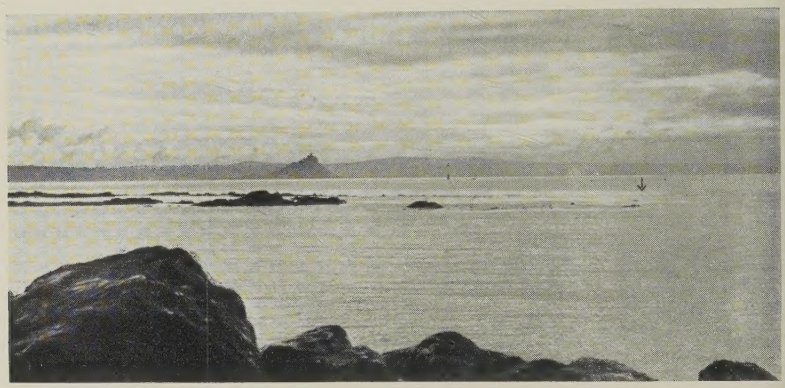

Fig. 1. View of the Wherry Rocks, with Lariggan Rocks in the foreground and St. Michael's Mount in the background. The site of the Wherry mine shaft is marked with an arrow at the farthest shoal. Photo by A. W. G. Kingsbury, 1948.

and dips north-west at an angle of 60° to 70°, and it was upon a stanniferous portion of this dike that the Wherry mine was sunk. The elvan, which is very variable in width, can be traced at low water from the Battery Wharf to Wherry Rocks, a distance of some 830 yards, but farther west towards Newlyn is not again visible (Boase, 1834). The map (fig. 2) is a reduced portion of the six-inch Ordnance map upon which has been marked the exact position of the elvan dike and the Wherry mine shaft. There is also some evidence that a definite lode intersecting the elvan was met with in the workings. The two mining prospectuses of 1834 and 1836 (further referred to below) mention a lode containing copper and a cobalt lode, the latter having a north and south direction; while William Jory Henwood writing of the mine in 1843 says that 'the masses and veins of the oxide of tin, which are distributed through it [the elvan] without regularity, rather appear to follow the intersection of the elvan by the Black lode'. This latter statement is tantalizing, for the nature of the Black lode is nowhere

mentioned. The mine, as will be shown, was worked at three periods.

First working.—Of this our knowledge amounts to little more than tradition. Early in the seventeen-hundreds it was known that one particular section of this elvan dike exposed at low tide was traversed by veinlets of very rich cassiterite, the adjacent rock also being more or

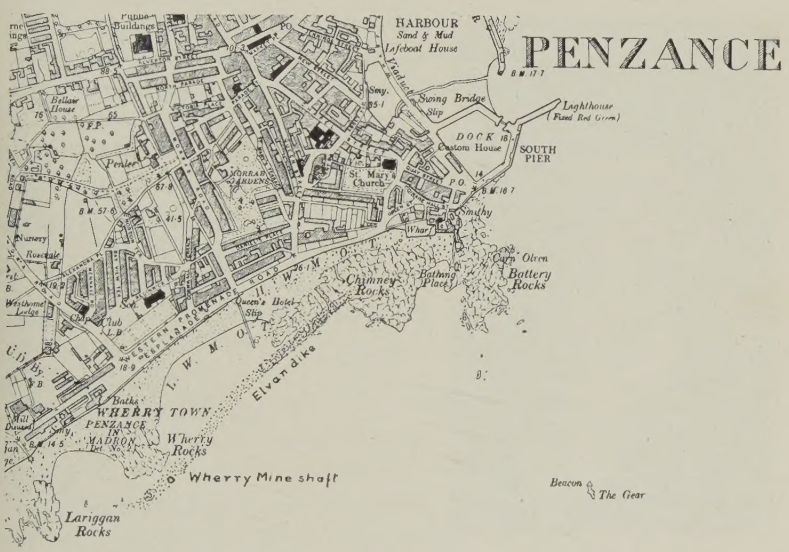

FIG. 2. Six-inch Ordnance Survey map, Cornwall 74 NW., second edition (1909), on which the positions of the elvan dike and the Wherry mine shaft have been marked. Reproduced ($\times \frac{2}{3}$) with the sanction of the Controller of H.M. Stationery Office.

less thickly charged with spots of the same mineral, and in consequence miners were tempted, when weather conditions and tide permitted, to remove the more easily accessible ore, until eventually the excavation so made, which according to Hawkins was few fathoms in depth, became untenable and the working was reluctantly abandoned to the waters. Ore-books of the old Angarrach smelting works contain entries of tin-ore bought in 1713 and 1714 from Penzance Work and Wheal Kathen, Penzance, either of which may well have been in the Wherry elvan.

Second working.—About the year 1778 Thomas Curtis (fig. 3), a working miner from Breage, then aged 57 and whose total property, Hawkins says, was not worth fifty crowns, became interested in the spot and conceived the bold idea of working it as a mine proper. With this end in view he commenced, apparently single-handed, to sink a very small

shaft practically on the site of the former workings on the shoal. In the winter months work was impossible and even in summer it was only practicable for two hours a day between tides, part of this precious time having to be devoted to bailing out the water. His difficulties may be gauged by the fact that the shoal is covered by the sea about ten months out of the twelve and at high tide the shaft collar was covered by 18 to 19 feet of water, and owing to the rapidly shelving beach, even at low tide the rock upon which the shaft was sunk was surrounded by a considerable depth of water, the spot moreover being prone to the breaking of much surf. One can imagine, too, his difficulty with blasting in so wet a situation when only black powder was in use and reeds or quills charged with powder were used in place of fuse. In this way three summers were patiently occupied, during which time the tin raised in the course of sinking can in no way have requited the labour. Whether from the commencement Curtis intended to work the mine by the plan he now proceeded to carry out, we know not, but it seems probable that he did. This consisted of preparing a flat hewn surface round the collar of his shaft, upon which was erected a turret of stout boards rising to a height of 20 feet above the rock and 2 feet 1 inch square, this apparently being the size inside timbers, so that the shaft was extremely small. The rock removed in preparing the foundation for this erection was dressed to shape and built round the outside of the base of the turret to form a collar, the whole being caulked with oakum and rendered with fat cement. The wood turret and the lagging of the shaft were also caulked and splayed with pitch. The turret was held in position by eight stout iron stays, four inclined from the four sides at the top to their hold formed by holes drilled in the rock, and four inclined from lower down and anchored in a similar manner. A platform of boards was then constructed round the mouth of the turret and this was lashed to four stout poles which were held in position by being

FIG. 3. Portrait of Thomas Curtis. (Artist unknown, but possibly John Opie.)

clamped to the turret stays. The platform itself afforded support for a windlass worked by four men.

The execution of this work, as might be expected, met with many mishaps and setbacks, but was after three summers successfully completed, and Curtis was then able to start regular production. He had apparently hoped that it would be possible to work throughout the winter except during very unfavourable weather conditions, but in this he was disappointed, for it was found that the swell and surf caused the water to find its way into the shaft, and when the workings were extended in a lateral direction a considerable quantity of water also found its way through the joints in the elvan, added to which when the sea was rough he could not transport his ore to the shore by boat.[1] The whole winter was therefore a period of inaction and it was not before April that the work could be restarted; when once resumed, however, the mine proved extremely rich and though worked on a very small scale only, became a most profitable adventure. Curtis had, however, apparently in common with many of the early coast miners, made the grave mistake of greedily attacking all available ore regardless of leaving an adequate rock and water barrier; and in the year 1789 he opened a pit on the shoal near his shaft and from it obtained tin worth £30.[2]

About twelve years after its commencement the mine was examined, in the autumn of 1790, by John Hawkins, who gives the following particulars. A short level from the shaft, which was then 26 feet deep, communicated with a large irregular chamber where the ground had been stoped away both above and below, leaving in places only 3 feet of rock between it and the sea, and heavy timbers were necessary to support the roof. The greatest depth of the stope was 36 feet, its maximum width 18 feet and minimum 3 feet, while owing to the dip of the elvan being as much as 60° to 70° the miners were actually able to walk up the foot-wall (Carne, 1822). At the commencement of each shift between tides, four men were employed for two hours at the windlass raising the water, apparently at the rate of four gallons a minute,[3] while towards the end of the time six men were 'teaming' or bailing the water from the bottom of the stope to the level from whence it ran to the sump. In

[1] The employment of a flat-bottomed boat or wherry for transporting the ore from, and materials to, the shaft before the erection of the trestle bridge was evidently the origin of the name Wherry mine.

[2] Letter from Samuel Milford to John Hawkins, dated Truro, March 11, 1834. (See below, p. 524.)

[3] In Hawkins's account in the Annual Register the amount of water raised is given as four tons a minute, tons being evidently a misprint for gallons.

Hawkins's second account of the mine, the number of men employed on the windlass is given as twelve, and this is probably to be accounted for by the fact that the work was so arduous as to necessitate frequent relays of four. The water having been got out the men then mined for a further six hours, making up a shift of eight hours. Between each tide they raised on an average, and landed by means of a boat, about thirty sacks of ore, each sack containing fourteen gallons.[1] Of this ore $\frac{15}{16}$ was so rich as to produce $\frac{1}{6}$ of a hundredweight of tin, the remaining $\frac{1}{16}$ producing $\frac{1}{16}$ of a hundredweight. The elvan where worked was 18 feet wide, 15 feet of it 'producing 1600 of "white tin" in 1000 sacks, and another foot as much as one cwt. of "white tin" in every sack'. In the six summer months of 1790 tin to the value of £600 was raised by the ten men employed. During Curtis's working, at any rate, the mine had no dressing appliances, the tin-bearing elvan being merely burnt in an ordinary lime kiln in order to render it more friable before being sent to a stamping mill.[2] A circular building which appears to be the lime kiln is shown on the engraving of the mine (pl. XXVI).

In the winter of 1791 Thomas Curtis died at the age of seventy, while the mine was steadily increasing in prosperity. His portrait reproduced here (fig. 3) is from a painting by an unknown artist, quite possibly John Opie (1761–1807), and has recently been presented to the Museum of the Royal Geological Society of Cornwall at Penzance by the late Dr. John Symons of that town.[3] John Hawkins records that in 1790 proposals were being considered for the erection of a lighthouse on the Wolf Rock off the Land's End and that he asked Curtis his opinion of the project, to which Curtis replied that he considered it practicable, but suggested as far preferable the blowing up of the entire rock, which he readily engaged to do for a proper remuneration. After Curtis's death the mine was apparently carried on by local adventurers, and Mr. Davies

[1] The very crude method of buying and selling tin ore by the sack was then still in vogue, the sacks being a convenient form of transport by mule or horse. The capacity of the sacks varied between 9 and 18 gallons beer measure, the buyer always reserving for himself a large margin for loss in dressing apart from the amount set aside for profit.

[2] J. H. Collins's statement (Observations on the west of England mining region, 1912, p. 68) that the ore was burnt because foul or contaminated with stannite, chalcopyrite, &c., is incorrect, for Hawkins specifically states the burning was to render it friable before stamping.

[3] I am informed by Dr. Symons's two daughters that they can offer no information as to how their father became possessed of the portrait; they have, however, two family portraits undoubtedly by Opie and the similarity of style suggests that that of Curtis may well be by that artist.

Gilbert, President of the Royal Society of London, in a letter[1] to John Hawkins dated September 1792 says: 'The course of stanniferous porphyry near Penzance (the Wherry) promises to make a very great mine. There are indications of the tin being continued to a great extent in both directions, and the bottoms are growing larger and remain rich. A house near the Green, built with fragments of this stone, which was probably picked up on the shore, or broken from the top of the rock, is, I hear, to be pulled down and rebuilt with other stone, for the sake of its tin. An adventurer told one that £3000 worth of tin had been raised from this extraordinary mine in the course of the present summer.' In a subsequent letter,[1] apparently also written in 1792, Mr. Gilbert says: 'A steam engine is erecting on the Green opposite, and they are constructing a wooden bridge from thence to the rock, to serve as a communication, till the engine shaft has been sunk sufficiently deep, and a drift carried out to the mine; as a stage for supporting the sliding or rather hanging rods.'

The engraving accompanying Hawkins's paper published in 1818 in volume 1 of The Royal Geological Society of Cornwall Transactions and reproduced here (pl. XXVI) shows this further important introduction of the engine, trestle bridge, and pump whereby the mine could be more effectively worked. The engine, a rotary, stood on the shore and, by means of flat rods carried along a wooden trestle-bridge, worked a Cornish pump in the shaft, the beam and balance bob of which can be seen in the engraving. On the authority of Mr. Joseph Carne (Carne, 1827) we learn that the engine was one of Mr. Jonathan Hornblower's two-cylinder compounds built in competition with the engines of Boulton and Watt, and was evidently one of the earliest if not the second of this type to be erected in Cornwall, the first being set to work at Tincroft mine, Illogan, in 1790 or 1791. A headgear was also erected over the shaft on the seaward side and this was apparently worked by a horse walking to and fro along the bridge, the animal being shown in the engraving, as also a man wheeling a barrow of ore or deads to the land. Whether the application of this machinery enabled the mine to be worked for a more prolonged part of the year is not known, but the probability is that it did. It is evident from Mr. Gilbert's second letter that it was ultimately intended to sink a shaft on the mainland and drive a level out to the elvan dike. This was, however, never done, probably owing to lack of capital and the usual failing of the old cost-

[1] Quoted by Hawkins in Trans. Roy. Geol. Soc. Cornwall, 1818, vol. 1, p. 141.

book companies, the desire to get what ore lay in sight with the minimum expenditure and time on dead work.

In 1794 the mine was visited by William George Maton, M.A., F.L.S., and Charles Hatchett, F.R.S., during their tour through Cornwall. In Maton's description of the mine, which he went down, he says it was then 17 fathoms deep, that the sea continually drained into the workings, and that the roar of it could be distinctly heard. 'The descent is by means of a rope tied round the thighs, and you are let down in a manner exactly the same as a bucket is into a well;—a well indeed it is, for the water is more than knee-deep in many parts of the mine. The upper part of the shaft resembles an immense iron chimney, elevated about twelve feet above the level of the sea, and a narrow platform leads to it from the beach: close to this is the engine-shaft, through which the water is brought up from below' (Maton, 1797). There are unfortunately no records of the mine during the next four years. In 1798, however, after a life of nearly twenty years, it came to an untimely end through an American vessel breaking its anchorage in Gwavas Lake (Newlyn harbour) and, striking against the turret, demolished the whole, thus ending this in every way remarkable venture. The staunch belief which Thomas Curtis always held for the mine, though he did not live to see it at its zenith, was expressed by him when he said 'There is more tin in the Wherry than would purchase all the land round Penzance', and in this he was to some extent justified, for during the twenty years of its working tin ore to the value of £70,000 was raised.

Third working.—In the year 1834 a prospectus headed 'Capital Speculation—The Wherry Mine, Mount's Bay' was printed by E. Heard of Truro. In this the former riches of the mine, which had lain abandoned some 36 years, are adverted to and extracts are given from the papers of John Hawkins and Sir Humphry Davy (Davy, 1818) relative to it. The presence of copper in the mine is also alluded to and the suggestion made that it could be profitably worked in conjunction with the tin. In corroboration of this it is stated that specimens of very rich copper ore had recently been picked up on the old dumps and that a lode of it had been left unwrought in the mine. It mentions that there were still some old men living in Newlyn who had made a 'comfortable independence' by taking tribute pitches in the mine during the former working. The prospectus also included a scheme for converting Gwavas Lake into a shipping basin. On the back of a copy of the prospectus in my possession, which is addressed to John Hawkins, is a letter to him from Samuel Milford, dated Truro, March 11, 1834, in which the latter says

he had lately inherited, through the will of his cousin Daniel Ley, a moiety of the Wherry mine and the estate adjoining, and asking Hawkins for his patronage and recommendations with a view to aiding the formation of a cost-book company for reworking the mine. According to this letter the mine at the time of its destruction in 1798 was 150 feet deep, and it mentions that Curtis always maintained that there was 'a good course of tin going west but only the rich branches followed down'. This company does not appear to have materialized until two years later when the two Cornish newspapers 'The West Briton and Cornwall Advertiser' and 'The Cornwall Royal Gazette', in their issue of April 29, 1836, contain a further prospectus and the notice of a meeting of the Wherry Mining Company held at the Union Hotel, Penzance, on April 25, 1836, with Mr. Richard Pearce[1] in the chair supported by Samuel Higgs[2] and Richard Millett.[3] The company consisted of 800 shares of £5 each.[4] In this prospectus, in addition to the tin and copper, mention is made of a 'large cobalt lode' running north and south. Unfortunately little or nothing is known of the work carried out by this company and I have failed to discover any record of the amount of tin, if any, which was produced. It is known, however, that success did not attend the venture and that the mine was finally abandoned in 1840 after a considerable loss. Whether, on reopening, the mine was found to be poor, or whether water and other difficulties precluded deeper and more extensive mining, or whether the very small capital was insufficient to place the mine on a sound footing, is not known. It is curious that again no attempt was made to sink a shaft on the shore and drive a level out to the elvan dike; however, the jointed nature of the slate rock and consequent likelihood of serious water difficulties, and Curtis's assertion that the deposit was more likely to yield riches in lateral extent rather than in depth, may have decided them against this course.

A now rare print entitled 'View of Penzance, and the Wherry mine, with the surrounding scenery', was drawn and published by James

[1] Richard Pearce (1792–1862) of Chapel Street, Penzance. Five times Mayor of Penzance.

[2] Samuel Higgs (1794–1874) of Alverton, Penzance. Grocer and merchant; he held an interest in a large number of mines and was purser of several in St. Just and Lelant, and Mayor of Penzance.

[3] Richard Millett (1807–85), solicitor, of Lariggan, Penzance.

[4] Mr. Ferris of 49 Belgravia Street, Penzance, has recently shown me a certificate for two shares of five pounds each in the Wherry Mining Company, Penzance, dated May 2, 1836. This certificate bears a receipt for two pounds as the sole and final dividend on the winding-up of the company by Mr. J. G. Beckerleg (Secretary), May 11, 1842.

Tonkin of Penzance about the year 1837 or 1838 (pl. XXVII); it clearly shows the layout, which differed little except in detail from that employed in the second working. A Cornish rotary engine, apparently not the original Hornblower, was erected on the shore, and by means of a trestle bridge carrying flat rods, worked a pump on Curtis's shaft which was again surmounted by a turret. There is also in my possession a small etching ($5\frac{3}{4} \times 8\frac{7}{8}$ inches) of Penzance and the Wherry mine signed as drawn and etched by A. M. S. Poltair. A. M. S. stands for Anna Margaretta Scobell, an artist of considerable merit, who was the only daughter of Captain Edward Scobell of Poltair, Penzance. In 1839 she married Daniel Higford Davall Burr, M.P., of Aldermaston Court, Berkshire. As can be seen from the accompanying reproduction (pl. XXVIII), the drawing was made from the foreshore directly west of the mine with Lariggan Rocks in the foreground, and differs considerably from and lacks many of the details shown in Tonkin's print. Though undated, the etching was apparently executed at the time of, or at any rate soon after, the last working from 1836 to 1840.

On September 25, 1930, the late Mr. E. Richards and his son, enterprising photographers of Penzance, succeeded on an exceptionally low tide in taking two photographs, one showing the iron pump column which still stands in the shaft, on this occasion 3 feet 6 inches above the surface of the sea, and another, the remains of two of the trestle bridge timber supports and iron tie-rods, both these photographs being reproduced in a paper on 'Abandoned Cornish mines' by the late Mr. E. W. Newton (Newton, 1930). In March 1948, on the occasion of an exceptionally low spring tide, I myself was able to wade out to the large pump column (18 inches diameter) which stands in a cup-shaped depression on the site of the old shaft, and my companion, Mr. Arthur Kingsbury, was able to take the photograph with part of Newlyn in the background which is reproduced in fig. 4. These scanty remains are now the only visible evidence of the mine, all traces of the dump having been buried long since under the concrete esplanade which was constructed by the Penzance Corporation in 1843. The account house of the mine is said to have stood at a spot now occupied by a café on the north side of the street.

The elvan dike and the minerals contained therein.

Although stanniferous elvans have been worked in a number of mines in Cornwall none is more interesting and remarkable than that of the Wherry mine. The rock forming that portion of the elvan dike on

which the mine was worked and which constitutes the outer portion of the shoal visible only at low tide consists of a groundmass of pinkish fine-grained orthoclase with sparsely distributed phenocrysts of quartz and innumerable small cavities plugged with scaly crystals of secondary chlorite and occasionally minute prisms and radial aggregates of dark brown to black tourmaline. Stanniferous phenocrysts and strings of translucent reddish-brown resinous cassiterite are sometimes sparsely and in other cases very thickly distributed.

FIG. 4. View of the iron pump column standing on the site of the Wherry mine shaft, with part of Newlyn in the background. Photo. by A. W. G. Kingsbury, 1948.

In another variety of the elvan the pinkish-buff groundmass of orthoclase contains innumerable small cavities, many of which are rudely square in outline, lined with minute pink adularia-habit crystals of orthoclase upon which are rosettes of dark green scaly six-sided crystals of chlorite beautifully iridescent on their edges, these also being accompanied by occasional slender prisms of black tourmaline. Distributed through portions of the elvan are large and small patches of dark green fine-grained chlorite which is in some cases highly stanniferous. More rarely the groundmass of the elvan consists of white felspar thickly spotted with round and square chlorite-packed cavities, while some are occupied by a single

square prism of cassiterite. Good specimens particularly of the pinkish-buff coloured elvan showing visible cassiterite may still be obtained from the dike outcrop close to the shaft site.

Cassiterite.—The Wherry mine cassiterite both massive and crystallized, of which unfortunately not many specimens have been preserved, is very characteristic of the locality, and R. P. Greg and W. G. Lettsom (1858) especially refer to the crystals as being both beautiful and remarkable, although by a curious error their description of the mode of occurrence is that of the cassiterite in the well-known slate and chlorite pebble conglomerate from Relistian mine, Gwinear. Most of the specimens herein described are from the Philip Rashleigh collection, the MS. catalogue of which contains ten entries of cassiterite from the Wherry mine, and of these the greater part are now in my possession, the remainder being in Truro Museum. The most characteristic type of ore, exemplified by two specimens raised in 1789, consists of pink elvan which is actually almost pure fine-grained mottled dark and light pink orthoclase with little or no quartz, and through which is disseminated much reddish-brown to black resinous cassiterite both in spots up to 6 mm. in diameter, often showing square and six-sided sections, and in strings. In other specimens the orthoclase groundmass is white, the thickly speckled cassiterite affording a striking contrast (fig. 5); in others again the felspathic rock is so densely charged with cassiterite as to impart a resinous brown colour to the whole mass. In a quite different type of ore, black cassiterite forms definite veins up to $2\frac{1}{2}$ cm. in thickness, composed of large intergrown pyramidal crystals, the walls consisting of white orthoclase heavily charged with disseminated cassiterite and chlorite, and it is in cavities in these veins that the crystals about to be described occur. Another type of ore consists entirely of fine-grained dark green chlorite through which are disseminated minute slender pyramidal crystals of cassiterite, the specimens often containing smaltite and showing crusts of erythrite. Two distinct types of crystals occur:

Type 1 (fig. 6 A and B).—Those of pyramidal habit, the so-called 'sparable tin', of which the Wherry mine crystals are the largest examples of this type of crystal known from Cornwall. They are exemplified by two very fine specimens, one from the Philip Rashleigh collection entered in the MS. catalogue as 'Tin Ore No 410. An Exceeding Rich piece of Tin Ore with Crystals $1\frac{1}{2}$ inch in length with long four sided & some six sided Pyramid Ends the points bursting into several Angles. Huel Wherry W R [William Rashleigh] r r r [very very rare] 1798.' The

other from the George Croker Fox collection consisting of similar but sharper and more brilliant crystals up to 1 inch in length. These crystals, which are black, are characterized by the prominence of the pyramid (321) in combination with (110), (320), (111) and sometimes (101). The prism faces are always deeply furrowed from the repetition of (110) with (320); and as a rule the crystals are considerably flattened parallel to the

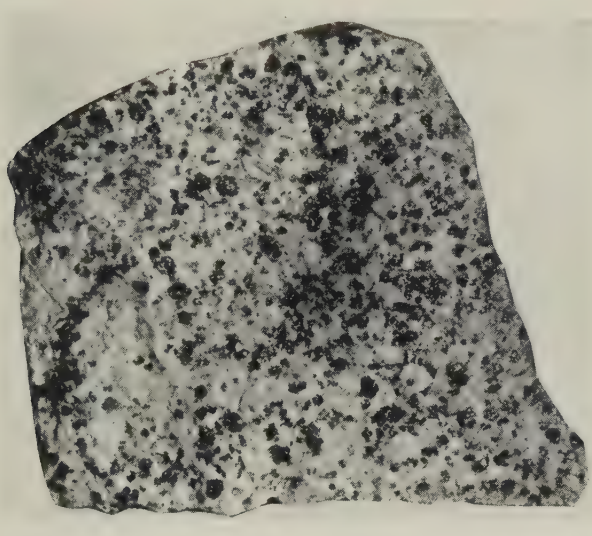

Fig. 5. Cassiterite disseminated in elvan. Philip Rashleigh collection, MS. catalogue: 'Tin Ore No. 345. Small spots of Black Tin Ore in White Quartz and Felspar, Huel Wherry near Penzance.' Natural size.

vertical axis and polysynthetically developed, a number and often a very large number of distinctly terminated crystals being united in parallel position to a common prism. A beautiful example of this is shown in a stout detached crystal $2 \times 1\frac{1}{4}$ cm., now in my collection, and which is probably the original of that figured and described in Philip Rashleigh's 'Specimens of British minerals', Part 1, 1797, pl. xxxii, fig. 14.

Type 2 (fig. 6 c and d).—Crystals of this type are characterized by the more usual prominence of (111) and (101) terminating a square prism (110). Fig. 6 c represents a crystal from a specimen from the Philip Rashleigh collection, the MS. catalogue entry being 'Tin Ore No 447. Tin Ore of a brown colour spoted with green Peach and Quartz, crystallized on the surface in the hollow part of which the crystals are

very perfect and curiously form'd. Wherry. W R.' These crystals are translucent, of a red-brown colour, and exceedingly bright and measure up to 7 mm. along the vertical axis. Upon them are several small white crystals of orthoclase of adularia habit and also minute rosettes of chlorite. They are further characterized by quite largely developed (430) in the prism zone, and the presence of (552) which appears as a

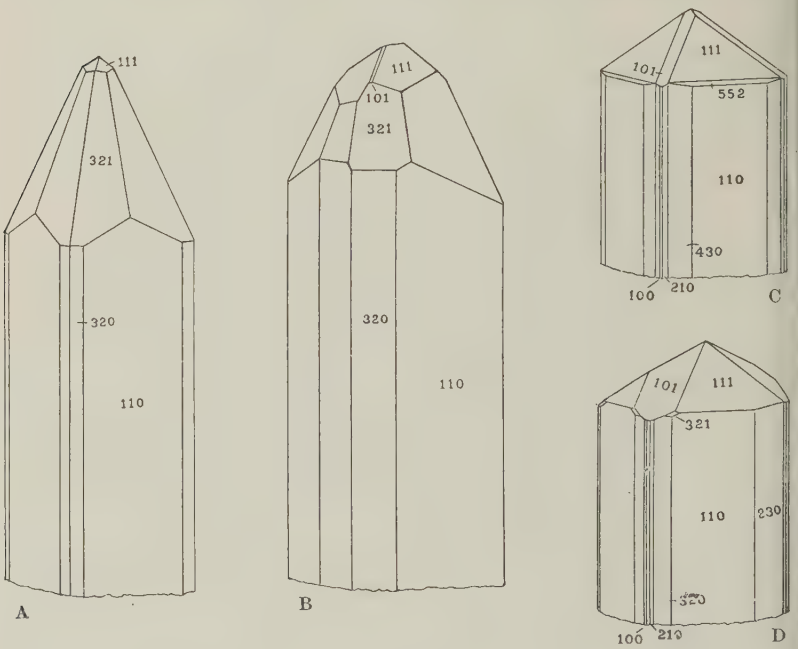

Fig. 6. Crystals of cassiterite from Wherry mine, Penzance, Cornwall.

bright and very distinct form but with broken continuity owing to the furrowing of the prism faces by alternations of (110) with (430) and (210). The other forms present are (100), (111), and (101). The largest of the crystals on this specimen are polysynthetic, a single prism having several distinct terminations. Two of the smaller crystals are beautifully twinned on (101), the only examples of twinned crystals I have seen from this mine. Fig. 6 D represents a measured crystal detached from a specimen from the Philip Rashleigh collection in Truro Museum. These crystals are black and attain a length of about $4\frac{1}{2}$ mm. and are considerably flattened, the forms present being (100), (110), (210), (320), (101), (114), (111), (552), (321), and somewhat doubtful (12.12.1). The

form (114) is nearly always present as minute faces terminating the crystals, but is not shown on the drawings. As in type 1 the (110) faces are deeply furrowed from repetition with (320). Face indices given above are for the axial ratio $a:c = 1:0{\cdot}6723$.

Chalcopyrite.—A good deal of chalcopyrite appears to have occurred, especially as the mine deepened, and W. G. Maton noticed it as being mixed with cassiterite in a quartzose matrix when he visited the mine in 1794. Sir Humphry Davy also mentions its occurrence, as does William Phillips; and in the prospectus issued in connexion with the third and last working the Wherry is spoken of as a tin and copper mine, and mention is made of there being 'a course or lode of copper ore left standing in the bottom 25 fathoms'. The only specimens I have seen are two from the last working, which were presented to the Museum of the Royal Geological Society of Cornwall, Penzance, by Mr. Richard Pearce, the chairman of the company. These consist of ordinary massive chalcopyrite with galena, chlorite, and quartz. In my own collection is one which shows a thin layer and an indistinct crystal of chalcopyrite on the surface of a very rich mass of resinous cassiterite distributed through white orthoclase with a little chlorite.

Galena.—This occurred in small quantity. There are two specimens in the Royal Geological Society of Cornwall Museum, Penzance, presented by Mr. Richard Pearce. One consists of a coarse cleavage mass, the other of galena associated with chalcopyrite in chlorite. In 1948 I found on the beach directly opposite the mine a large rolled pebble consisting of light brown chalybite traversed by a vein of quartz and containing several patches of galena. Whether this actually came out of the mine is uncertain, but if it did, it is evidence that there is a true lode in addition to the stanniferous elvan.

Blende.—This is one of the minerals which Sir Humphry Davy states he found on the mine dump. I have not seen a specimen.

Arsenopyrite.—This is another of the minerals recorded as occurring here by Sir Humphry Davy, and I have a specimen from the Lady Elizabeth Anne Coxe Hippisley collection, which was presented by him to that lady prior to 1818. It shows a number of tolerably well-defined tin-white crystals up to 6 mm. in length, combinations of (110) and (014), vertically flattened, and embedded with some quartz in compact greyish-green chlorite.

Smaltite.—Mention has already been made of a 'cobalt lode' having a north and south direction being met with in the workings. A specimen from the Philip Rashleigh collection in my possession labelled 'Rich

Cobalt ore, Wherry mine', and also one from the Lady Hippisley collection presented by Sir Humphry Davy, show crusts of erythrite on fine-grained chlorite thickly charged with cassiterite, and on freshly fractured surfaces small granular patches and disseminated grains of tin-white smaltite. The Davy specimen, according to the label, contains nickel in addition to cobalt, as nearly all smaltites do, and in the list of minerals which he recorded having found on the Wherry dump, nickel is included. Robert Hunt writing in 1887 says that there was a tradition of an attempt to utilize the ore for the manufacture of smalts and goes on to say that within the last few years good specimens of tin-white cobalt [smaltite] have been collected from crevices of the rocks a short distance above low-water mark, between Penzance and Newlyn.

Erythrite.—Three specimens which I have from the Philip Rashleigh collection and one from the John Hawkins collection presented by Philip Rashleigh, and also one from Lady Hippisley's collection presented by Sir Humphry Davy, show crusts of erythrite in the form of minute globules of a peach-blossom colour on fine-grained chlorite heavily charged with cassiterite and some smaltite. Accompanying the erythrite are very small quantities of a white to yellowish efflorescent substance—a sulphate, apparently alunogen.

Pitchblende.—Sir Humphry Davy mentions having found 'pechblende' and 'oxide of uranium' on the Wherry dump. The 'oxide of uranium' may have been either torbernite or autunite as at that date both these minerals were assumed to be oxides, the latter a pure oxide of uranium. As far as I am aware no specimen of any uranium mineral from the Wherry mine has been preserved.

Sir Humphry Davy also mentions having seen on the dump 'oxide of titanium and iron' [ilmenite]; and T. M. Hall (1868) gives cobaltite and wad as having occurred; the cobaltite is probably a mistake for smaltite and the wad needs confirmation.

Axinite.—As already mentioned, axinite occurs abundantly in lenticles and strings in the greenstone adjoining the elvan dike and may be found both in the water-worn boulders on the beach and in the Wherry and Lariggan Rocks. It is coarsely crystalline and has the usual violet-grey colour, but seldom shows definite crystals: it is accompanied by small quantities of yellowish epidote, actinolite, and sometimes a little pyrite.

Sir Arthur Russell: The Wherry mine, Penzance.

Sir Arthur Russell: The Wherry mine, Penzance.

Sir Arthur Russell: The Wherry mine, Penzance.

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Explanation of Plates XXVI–XXVIII.

Pl. XXVI. Wherry mine, Mount's Bay, Cornwall. St. Michael's Mount in the background. Reproduced from the frontispiece of vol. 1 of Trans. Roy. Geol. Soc. Cornwall, 1818.

Pl. XXVII. Reproduced from a rare print entitled 'View of Penzance, and the Wherry mine, with the surrounding scenery', drawn and published by James Tonkin of Penzance, about 1837–38.

Pl. XXVIII. View of the Wherry mine and Penzance. Reproduced from an etching by Anne Margaretta Scobell, about 1836–40.

Goethe's interest in British mineralogy.

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[Communicated by L. J. Spencer; read by C. E. N. Bromehead, January 27, 1949.]

JOHANN WOLFGANG VON GOETHE (1749–1832), the bicentenary of whose birth at Frankfurt-on-Main will be commemorated on August 28, 1949, gave us extensive accounts of the development of his studies in optics, botany, and meteorology; with regard to the history of his studies in mineralogy and geology, his most concise statement is his essay 'Geology, in particular that of Bohemia'. This essay, written in 1817, starts with three quotations. The first is in English:

> What is the inference? Only this, that geology partakes of the uncertainty which pervades every other department of science.

The source of this quotation still remains to be discovered. At the end of this essay, Goethe said that he was:

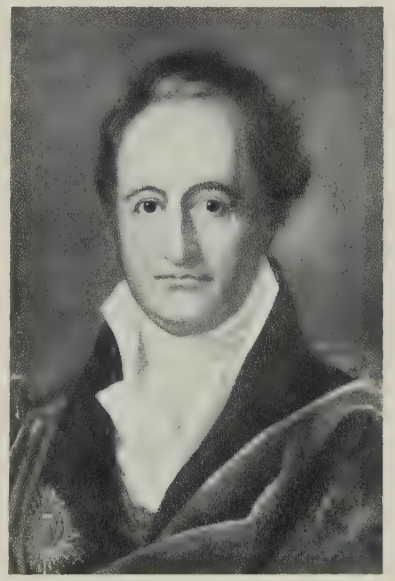
> fortunate in obtaining a series of minerals from all the principal countries. Herr Mawe, the mineral merchant in London, provided me with a most satisfactory collection from Cornwall, and to Herr Ritter v. Giesecke I am indebted for an important addition to my collection of English stream tin and Malacca tin. All these materials have now been well arranged in my collection, but my plan to write something conclusive on this subject could not be carried out, as so many other things I should have liked to do in the scientific field.

In the 1833 edition of Goethe's works the section of his mineralogical and geological writings concluded with his review of John Scafe's poem 'King Coal's levee' (4th edition, London, 1820), and this arrangement has been preserved in most editions of Goethe's works.

It is a well-known fact that Goethe's 'Theory of colours' is mainly a discussion of Newton's teaching; in the historical part of that work, no nation figures more prominently than does the British nation. In Goethe's botanical studies Robert Brown occupied an important place, and his meteorological studies were chiefly inspired by Luke Howard and J. F. Daniell. While Goethe clearly acknowledged his indebtedness to British scientists also in the mineralogical field, it has never been established what knowledge of the mineralogy of Britain was conveyed

to him through those contacts. It may be regarded as providential that as early as 1806 Johann Georg Lenz (1748–1832), the mineralogist at Jena, chose the name of goethite for a mineral, the best crystals of which come from Cornwall.

Shortly after writing his essay 'Geology', Goethe stated that his interest in mineralogy dated from his twenties. Among his earliest notes on this subject we have a reference to 'Galmey, cubic hollow crystals, apparently pseudomorphs, from Flintshire' (Weimar edition, 2nd series, vol. xiii, p. 392). However, Goethe admitted at that time he was merely toying with scientific subjects.



J. W. von Goethe
(at the age of about 60)
From a painting by Luise Seidler in the Mineralogical Museum at Jena.

As in the meteorological field, in mineralogical studies his methodical interest was evoked through his patron, the Grand-Duke Karl August of Saxe-Weimar. In 1816, when touring England, the Grand-Duke had collected information on English minerals. On May 21, 1816, Goethe entered in his diary: 'The Grand-Duke had brought English books. Dinner at Court. Unpacked chrome-iron specimens.' On April 17, Goethe had forwarded to Lenz notes on the 'Suiten' the Grand-Duke had brought from England, and on the iron and coal deposits near Birmingham, which the Grand-Duke had specially studied. These notes, Goethe requested, should be 'placed with the other materials', apparently a collection of information on coal and ore deposits in other countries to be studied with regard to the development of the mineral resources of the Grand-Duchy of Saxe-Weimar (a subject to which Goethe devoted his attention as early as 1797, see Weimar edition 1st series, vol. liii, pp. 320 f. and 525). It is not impossible that the visit of 'three geological Englishmen', recorded in Goethe's diary of July 11, 1816, was connected with the Grand-Duke's tour.

It appears that the information supplied by the Grand-Duke coincided with a specific interest which Goethe had already conceived in the mineral resources of England. On November 11, 1815, he stated in his diary that in the morning and in the evening he studied 'English minerals'. In December 1814 he had written to C. C. von Leonhard, the mineralogist at Heidelberg, asking whether he could assist him in obtaining 'Zinnstufen' from England, which, he said, were still missing in his collection. Owing to the war Leonhard apparently was unable to help Goethe, for on June 23, 1817, Goethe asked Hüttner, the book agent of the Weimar Court in London, to procure for him

an instructive series of English tin formations. What is required, are not expensive and extraordinary pieces, though beautiful specimens among the instructive ones would be acceptable. The main interest is in both the nearest and the more distant strata. In Wallis [i.e. Cornwallis] as everywhere else, tin occurs in what is only apparently granite; it would be desirable to obtain specimens of the more distant original stratum, even when it is several hours distant. I do not dare to place an order, because, due to the trouble involved in the collecting of such specimens and the total absence of any standards of remuneration, such an order could not be made sufficiently definite. If it would be possible to give me an approximate idea as to the costs of obtaining such a collection wherever it may be, the details of the order could then be decided upon.

I suggest that this letter is an important record of the organization of the work of the early mineralogists.

Perhaps it was in connexion with Goethe's request that Hüttner obtained for the Weimar Library a copy of 'A descriptive catalogue of minerals' (2nd edit., London, 1816) by John Mawe, which Goethe borrowed from September 5, 1817 to July 20, 1818 (in his diary for September 6, 1817, referred to as 'Mawes Catalog').

Towards the end of September 1817, Goethe wrote to Lenz asking him whether

Herr G. [*sic*] Mawe, author of the 'Mineralogy of Derbyshire, Travels in Brazil, Treatise upon Diamonds, and others [*sic*] Precious Stones' should receive a diploma [of membership to the Jena Mineralogical Society], if not [Goethe obviously meant: 'if so'], I request that it should be speedily issued.

On October 23, Goethe's diary refers to 'Mawes Edelsteine' and on the next two days to 'Mawes Demanten' (read in conjunction with Lenz's manual of mineralogy), again on November 16, 1819, 'Mawe Abhandlung von Diamanten'. (Goethe's borrowing the German translation by C. G. Kühn (Leipzig, 1816) of Mawe's Treatise is recorded in the Weimar Library for October 24 to December 20, 1817 only.)

On November 4, Hüttner wrote to Goethe that

the diploma of the Mineralogical Society has given great pleasure to this truly worthy man, as is proved not only by his letter of thanks (which is enclosed), but also by the account, specially compiled by him for that Society, of his late tour in Cornwall. These notes on the remarkable Bovey coal works have never been published. . . . He continued in his letter [to Hüttner]: 'Any thing this Country or Brazil produces and which I either possess or can procure, I am willing freely to exchange for the mineral productions of the Continent.'

On November 27, Goethe's secretary dispatched to his master, then at Jena, by express mail the copy, obtained on loan from the Weimar Library (until July 4, 1818), of the German translation of Mawe's 'Travels in Brazil' (Bamberg, 1817), by E. A. W. Zimmermann, a friend of Goethe's. Apart from W. L. von Eschwege, also a friend of Goethe's, Mawe had been the first scientist to obtain permission from the Portuguese government to study the mineral resources of Brazil. There is evidence of the impression which Mawe's 'Treatise upon diamonds' made on Goethe. When on June 20, 1819, he thanked Pansner, the mineralogist at St. Petersburg, for sending him some amethysts, Goethe asked him to extend his studies to a comparison with similar minerals in England. In his letter to Sir Charles Giesecke of November 22, 1819, Goethe stated that he had learnt from Mawe's work that citrine was found in Cairngorm in Aberdeenshire.

Hüttner's letter of November 4, 1817, with the enclosures from Mawe, was received by Goethe on November 24, when the whole day was spent in a preliminary study of Mawe's essay, in meditations upon its contents and the prospects opened by this contact, and in discussions of these subjects with friends. Goethe's diary entry for this day concludes: 'In the night deciphered, and meditated upon, Mawe's essay.' On the following day, Goethe proceeded to 'translating Mawe's essay on the brown coal deposits of Bovey', and three days later he wrote to his son that

Herr Mawe feels greatly honoured by our diploma. We may expect the best from him. That winter day, which will bring me 'Zinnstufen' from Cornwall, shall be marked in red. In general, the study of this subject has become so clear that I can hope my ideas will be realized almost by themselves.

Goethe's meditations upon the contents and implications of Mawe's essay and the general conclusions he drew from it illustrate the philosophical manner in which he dealt with scientific details. This incident further illustrates the eagerness with which Goethe used to receive and assimilate information, especially in the scientific sphere, obtained from Britain. How conscientiously he proceeded may be seen from the fact that when, on December 17, he found the time to resume his work on

Mawe's essay, he first revised the first part of his translation before translating the rest; on the same day he discussed mineralogical subjects with Lenz. Early in 1818, Goethe submitted his translation to the Jena Mineralogical Society, adding the following 'Note and wish':

The Jena Mineralogical Society, especially its president and council, have learnt with great pleasure of the interest which Mr. Mawe is willing to take in its work. The account of his latest expeditions has been translated at once into German, and a copy of this translation is enclosed. Perhaps Mr. Mawe would examine it with the assistance of a person who knows both English and German and would inform us whether we have interpreted him correctly. This account would then be inserted into the proceedings of the Society. (Weimar edition, loc. cit., pp. 394 ff.)

It seems to be unknown whether Mawe revised Goethe's translation, and there is no indication either that the original of Mawe's essay has been preserved. It was not until 1823 that the 'Annalen der Societät für die gesammte Mineralogie zu Jena' (of which four volumes had appeared between 1802 and 1811) resumed publication under the title 'Neue Schriften der Grossherzoglich S[ächsischen] Societät für die gesammte Mineralogie in Jena'. Only two volumes appeared, in 1823 and 1825 respectively, and Mawe's essay is not found in either of them.

Considering the hesitancy with which Goethe released his translation of Mawe's essay, it requires some courage to offer a retranslation. However, with the recent publications on the lignite of Bovey Tracey and the interest lately taken in the industrial utilization of these deposits, my undertaking may be justified. 'Mr. Mawe's account of his late expeditions in October 1817' starts with a reference to Cornwall, Devonshire, and Exeter. It then concentrates on Bovey, 'a village in the east of Dart Mon' [*sic*]. I confine my retranslation to the passages of mineralogical interest:

The clay has stripes of various whiteness, usually of a light smoke colour. When burnt, it is pure white and after some preparation yields a splendid product. In the north and even more so in the west, we have granite minerals, especially the variety known as 'Monstein' which is richer in felspar than are other varieties. This felspar is now gradually decomposing. In the north, mountains of clay-slate, and syenite are rarer than those of granite. The plain covered by that clay has formed at the foot of the granite Dart Mon [*sic*] mountain. On the west side only a few feet below the surface is a deposit, about two miles wide, of a special variety of coal. It is covered by a layer of shale with bitumens (known as 'fuel slate'), friable and liable to decompose, five to seven feet deep. This coal is won in open-cast mining, and is up to 50 feet deep, 25 feet are visible above the water which fills the bottom of the pit. This coal has the appearance of a large heap of decomposed manure, its colour varying from brown to blackish-brown, with a fine lignite structure towards all sides. Some parts show a perfect lignite structure. It is neither brittle nor shiny, rather dull; interspersed is resinous asphalt, easily inflammable and agreeable in smell. The coal is excavated by means of a sharp spade and an

edged tool. It yields considerable heat, with an unpleasant smell, so that it is used only in lime kilns and in the houses of the poor. At careful handling this coal can be cut into boards of any length and not above one inch in thickness. At drying, these boards become hard and brittle. This substance, so different from what the English are used to call 'coal', deserves special attention.

There is no limestone or other overburden as otherwise found with coal; there are no clay-ironstone fossil plants, pyrites, or other sulphurous materials, as generally found with normal coal-fields, no remnants of sea-shells, only the aforesaid clay and bituminous slate and some quartz layers. The formation of this coal is so different from any other, that it deserves the attention of geologists. It is excavated down to 55 feet. As the works are at the bottom of the mine, they are easily flooded.

It may be mentioned at this point that on July 15, 1827, Goethe noted in his diary a reference to 'British Chronicle' (xxv, 1827), 'News of mining in Cornwall and Mexico'. With regard to Mawe's reference to the absence of fossil plants, two English items in Goethe's studies in fossil formations may be of interest. In April 1817 he translated from 'Annals of Philosophy' (1816, no. 144, p. 153) a note by one R. Y. on finds in prehistoric tombs 'opened by order of the British commanding officer, at Cephalonia'; this translation is an important record of Goethe's knowledge of English geological terminology. With regard to that account, Goethe said that its 'tact' in being 'satisfied with natural explanations' was exemplary, one of the earliest appreciations by Goethe of an English scientific text. On March 30, 1826, Goethe read E. T. Artis's 'Antediluvian Phytology, illustrated by a collection of the fossil remains, peculiar to the coal formations of Great Britain' (London, 1825), a work paying high tribute to German workers in the field, especially Count Sternberg, Goethe's mineralogical friend, and acknowledging its indebtedness to Noehden, one of Goethe's most important informants on England.

To come back to Goethe and Mawe, following the latter's suggestion to establish an exchange of minerals, Goethe carefully prepared for him a collection of minerals, chiefly from the Rhineland, and extensively indexed, labelled, and packed it; this collection was dispatched in July 1818. Referring to this collection in his report to the Jena Mineralogical Society, Goethe, curiously enough, did not say that he sent it in exchange for what Mawe had sent him. Reviewing his activities in 1817, however, he said that through Mawe's book on Brazil he obtained information of those parts of the world.

As for myself, I entered into personal contact with Mawe, receiving through his good offices a fine collection of English "Zinnstufen", as always [namely, as the specimens from other parts of Europe in Goethe's collection] obtained from the immediate vicinity of primitive rocks [granite], this time in chlorite minerals.

These were obviously not the 'Englishen Stufen', the receipt of which Lenz reported to Goethe on July 22, 1817. In 1827 Goethe again referred to his collection of tin formations 'from Sweden, Spain, and England' (in a letter to a mine official at Altenberg, in the Ore Mountains of Saxony, who was naturally interested in this subject).

Even before establishing relations with Mawe, Goethe had come into contact with scientific mineralogy in Britain. On March 22, 1817, he had written to Voigt (of whom more below):

I enclose an issue of the English journal edited by James Sowerby, showing instructive specimens and excellent illustrations on plates 43, 44, and 45. In return, he should receive a diploma, many thanks, and further requests. This issue will generally please your Excellency. The whole work will be obtained, the copper plates being most acceptable substitutes for the originals.

This was evidently no. 8 (June 1812) of James Sowerby's 'Exotic mineralogy' (2 vols., issued in 27 parts, London, 1811–20), where plates 43–45 show corundum, specimens of which had been received by Goethe on March 21, 1817. On the title-pages of vol. 5 (1817) of 'British mineralogy' and vol. 2 (1818) of his 'Mineral conchology' Sowerby figures as Honorary Member of the Mineralogical Society of Jena, but as he died in 1822, his name does not appear in the Society's list of 1823.

The high quality of copper-plates and hand-colouring in English books was frequently admired by Goethe; Sowerby's work was known to him from the early volumes of Curtis's 'Botanical Magazine', and from Sowerby's 'Elucidation of colours' to which he repeatedly referred. In 1822 he borrowed from the Weimar Library W. E. Leach's 'Malacostraca podophthalmata Britanniae' (London, 1815), which, with reference to the illustrations, he described as 'Sowerby Malacostraca'.

However, it was by no means only the external appearance of English scientific books that appealed to him.

In 1826 Goethe read Mawe's 'New descriptive catalogue of minerals' (fourth edition, London, 1823); while 'meditating upon the smallness and comprehensiveness of such manuals', Goethe realized 'the heaviness and clumsiness' of similar German works, a significant statement of Goethe's opinion of British scientific writing in general.

In the spring of 1819, Goethe met, at a meeting of the Jena Mineralogical Society, Joseph Green Cogswell, mineralogist and librarian at Harvard University. Among other books on America, he received from him Wm. Maclure's 'Observations on the geology of the United States of America' (Philadelphia, 1817) and 'Observations on the geology of the West Indies' (Journ. Acad. Nat. Sci. Philadelphia, 1817, vol. i, part 1); both works are still in Goethe's library. Through Cogswell, Goethe sent, on July 29, a diploma of membership of the Mineralogical

Society to Parker Cleaveland, in return for a copy sent to the Society of his 'Elementary treatise on mineralogy and geology' (Boston, 1816). This book, the first work of its kind in America, was alternatively referred to by Goethe by its title in German translation as 'Amerikanische Geologie', 'Mineralogie', or 'Geognosie der Vereinigten Staaten', the last title rather surprisingly, as otherwise Goethe insisted on the distinction between geognosy and mineralogy. Cleaveland appears in the list of foreign members in vol. i of the 'Neue Schriften' of the Jena Mineralogical Society; in vol. ii, his name appears among the foreign honorary members; and the second edition (1822) of his work (on the title-page of which Cleaveland described himself as 'Fellow of the Mineralogical Society of Jena') is listed among the accessions to the Society's library; of this edition Goethe spoke extensively in his letter to Count Sternberg of June 20, 1826. In the spring of 1826 Goethe read the work of another American scientist, namely 'Narrative of an expedition to the source of St. Peter's River' (London, 1825) by Wm. H. Keating; especially on March 24 he noted: 'Compared Keating's Journey through North America with a map'. These relations between Goethe and American mineralogists should be studied with a view to establishing Goethe's knowledge (rather than his opinion) of America. With regard to American minerals, Goethe's knowledge was not confined to mere reading; in his essay on 'Zinnformationen' (written in 1813, Weimar edition, 2nd series, vol. x, 121), he mentioned 'Tropfzinn aus Cornwallis, aus Amerika'.

In 1820 Goethe opened for himself another important source of information on British mineralogy. On March 24 he received from the Weimar Library 'new English books', one of the numerous consignments sent by Hüttner; the evening of the following day was spent in the study of these books. On March 26 and 28 he definitely referred to his reading Macculloch's 'Westliche Inseln Schottlands.' On March 25 he wrote to Bran in Jena that, in compliance with his request to send him new English books of possible interest to his ethnographical periodical, he returned to him two of these newly arrived works, one on the Antilles and one on Nubia, retaining Macculloch's, as, from the table of contents, it appeared to deal exclusively with mineralogy. (Later he discovered that the scope of this work was much wider.) On March 28 he wrote to the Grand-Duke:

The last consignment of English books was very important. . . . I am studying with great interest Macculloch's 'Westliche Inseln'. It is curious and agreeable for us old Neptunists that the words 'volcano' and 'volcanic' do not occur in this book, and that basalts are reckoned, in accordance with Werner's good custom, to the Trap formations.

Long after A. G. Werner's death (in 1817) Goethe and the Grand-Duke of Saxe-Weimar adhered to his neptunism, chiefly against plutonism as represented by Hutton and later by A. von Humboldt. In Thuringia, volcanism was supported by J. C. W. Voigt, the mineralogist at Ilmenau, a former pupil of Werner's. Referring to his controversies with Voigt, Goethe wrote on March 31, 1820, to Nees von Esenbeck, a mineralogist greatly admired by him:

As God has mercy on those who believe in Him, just when their distress is greatest, a work has reached me, from which I gather that beyond the sea at least there are still fellow adherents to the old creed. 'A Description of the western Island's [*sic*] of Scottland' [*sic*] by John Macculloch, London, 1819, two volumes text in 8°, the third in 4° with engravings and copper-plates, is an excellent work in every respect; closest observation of the formation of islands, partly from nature, partly raised to general conceptions and symbolical images. Of course, the sections of islands are more convenient for this type of study than are the solid masses of the continent. (Weimar edition, 4th section, vol. xxxii, p. 372.)

While admitting that he was biased in favour of this work because it was written from the neptunist point of view, Goethe concluded: 'At any rate, this work can be warmly recommended to any lover of nature, whatever his scientific creed may be.'

Only a few months later, Goethe received a further striking proof of the survival of neptunism 'beyond the sea'. On November 19 he wrote to the Wernerian Society at Edinburgh to thank it for the diploma of honorary membership which had been sent to him with a hand-written letter from Robert Jameson, its president. Only those who are unaware of Goethe's extensive interest in British mineralogy can doubt (with Leitmeir) 'whether this honour was conferred upon Goethe in his capacity of mineralogist or of poet'. In 1823 it was C. F. Schwägrichen, the botanist, who procured for Goethe the membership of the Royal Society of Edinburgh (then under the presidency of Sir Walter Scott); and in 1825 Giesecke, professor of mineralogy at the Royal Dublin Society, was instrumental in having Goethe elected honorary member of the Royal Irish Academy. Among Goethe's notes from Nose's 'Kritik der geologischen Theorien' (1822), there is a paragraph on the Wernerian Society of Edinburgh:

which not only recognised the value of the great German and his school in general but also knew how to adapt his teaching to the progress of science. This Society and its president Jameson consider the two opposed theories of neptunism and plutonism, outlining the higher laws or demands of nature.

Also with regard to the western islands of Scotland, Goethe's mineralogical knowledge did not remain confined to reading. In October 1826,

Vargas Bedemar, the Danish chamberlain, on his return from Scotland, brought for the Grand-Duke's collection of precious stones some 'Scottish topazes' (a few years earlier he had brought precious stones from the Faeroes). These stones were at once submitted to Goethe for ascertaining their mineralogical rather than their material or aesthetic value, and writing on October 30 to the Grand-Duke, Goethe stated that he was interested in learning that

such stones are also found in those parts of the world; similar topazes have been found in Ireland. Thus the sequence and congruity of original rock formation all over the earth is once again illustrated,

a typical example of the conclusions, often perhaps too far-reaching, which Goethe used to draw from minor data. The minerals of Staffa and Fingal's Cave were also mentioned in John Scafe's 'King Coal's levee' and Goethe's summary of it, to which I shall refer presently.

In his letter of August 30, 1830, to Wackenroder, the pharmacologist at Jena, Goethe referred to a paper which, according to the official report, Leonhard had read at the meeting of German scientists at Heidelberg in September 1829 on the subject of 'verglaste Burgen', doubtless based on Macculloch's 'Remarks on the vitrified forts of Scotland' in 'Transactions of the Geological Society of London', 1814, vol. 2, pp. 255 ff. On December 24, 1830, Goethe received a copy of Leonhard's paper and on January 6, 1831, a few specimens of this formation; this information was communicated on January 22 to Mahr, the mine inspector at Ilmenau, an illustration of the important part which Goethe played in the promotion of German knowledge of the mineralogy of Britain (see also his paper on vitrified forts (Weimar edition, 2nd series, vol. x, pp. 43 ff.). With reference to Mawe's essay translated by Goethe, it may be of interest that in the same volume of the 'Transactions of the Geological Society of London' Macculloch had an article on distillation, relating also to Bovey lignite or brown coal.

There is no evidence of Goethe's reading the 'Transactions', but among the notes which he took from Nose's work there is a passage on the Geological Society of London and on Greenough, its President, who

point to the wrong methods in the formation of theories, but do not sufficiently state the right method. Greenough rejected the theories of both Werner and Hutton, but failed to throw new light upon the subjects.

Goethe then noted Nose's remarks on the works by Greenough and Macculloch. 'A critical examination of the first principles of geology' by G. B. Greenough (London, 1819) was mentioned in Goethe's diary of August 9, 1820. In his Annals for 1820 he said that the arrival of

this work 'from England was very welcome'. Once again he was biased in favour of the work by a British mineralogist because of its neptunist point of view: 'Though I have been accustomed for many years to hear Werner's views stated in a foreign language, this work has been both exciting and delightful to me.' Greenough had studied in 1798 at Göttingen under Blumenbach (on whom in 1840 he delivered an obituary address, praising him as 'the John Hunter of Germany') and subsequently at Freiberg under Werner. In 1811 he became the first president of the Geological Society of London, encountering some opposition from Sir Joseph Banks who wished to subordinate it to the Royal Society. Goethe was much interested in the organization of scientific societies in Britain, very well acquainted with the history of the Royal Society, and aware of Sir Joseph's various activities; in his letter to Sternberg of September 13 to 21, 1826, he referred to Cuvier's praise of Banks's mineralogical achievements. Greenough generously acknowledged his indebtedness to Werner and other German geologists, and most of the books which he presented to the library of the Geological Society were German. Re-reading his work with Goethe's eyes, one cannot fail to recognize that it was a source not only of the first principles of geology but also of the geology and mineralogy of the British Isles. Goethe also seems to have known Greenough's 'Memoir of a geological map of England' [and Wales] (1820), or it would appear that such a map, 'particularly extensive and neat' was included in his copy of Greenough's 'Critical examination' (it is not in the copy of that work which Greenough presented to the Royal Dublin Society, now in the National Library of Ireland). In his diary for July and August 1820, Goethe repeatedly speaks of a large geological map of England in his house, in which also the Grand-Duke and the Princesses were greatly interested. On the same day, when he received the Scottish topazes, mentioned above, Goethe asked the Jena Museum to send him 'the petrographic map of England', and in November 1828 he discussed with Eckermann 'the English geological chart'.

Through his extensive reading, Goethe had become thoroughly acquainted with English mineralogical terminology. In 1822, in his essay 'Kalk-Gebirg', mainly dealing with Thuringia, he specially discussed this subject, stating that '*Chalk* is in English not what we understand by it [*Kalk*, i.e. lime] but *Kreide*. If contained in *Letten-Flötze* it is called *clay*', and comparing the English terms 'red clay', 'black earth', and 'sand' with their German equivalents. The most interesting illustration of Goethe's knowledge of English mineralogical terminology

is his summary of John Scafe's 'King Coal's levee'. While Goethe's literary appreciation of this poem has been studied before, there is still room for an investigation into the contribution made by that work to Goethe's English scientific vocabulary. While in many cases no translation of the mineralogical terms was necessary (because these were either international or of German origin), the translations of 'limestone' by 'Urkalk', 'Lias' by 'Tuffstein', and 'chalk' by 'Flötzkalk' prove Goethe's intimate acquaintance with the subject. The passage: 'Chalk when at home was never seen without him' [flint] was expanded by Goethe to: '*Flötzkalk*, residing in southern England, was never found without this rogue', thus showing that he had knowledge of English mineralogy of his own. The notes which Scafe added to his curious poem were doubtless an important source of Goethe's information of the mineralogy of the British Isles. Shortly after writing his review of this poem, Goethe told Crabb Robinson that 'Scafe's "King Coal's levee" contains all the geology a man needs to know'. In the beginning of his review Goethe made the still more significant statement:

> The English nation is at a great advantage by the fact that her scientists try to make practical use as soon as possible of both their comprehensive theories and the individual details of their investigations. The safest way of doing so is by spreading knowledge as far as possible.

As late as March 1831, Goethe tried through John Murray, the publisher, to establish personal contact with Scafe.

On the strength of his reputation as a poet, Goethe succeeded in carrying information on scientific subjects into circles which otherwise would scarcely have taken any interest in them. Without such popular and practical interest the development of modern science cannot be thought of. While the attempt sometimes made to describe Goethe as a great discoverer of scientific facts and theories, such as the glacial period, cannot be excused, it is hard to be patient at the harsh verdicts frequently passed on amateurish activities. Such criticism is expressive not only of lack of historical perspective, but even more so of ingratitude towards the pioneers of mineralogy. By his adherence to Wernerianism, Goethe was in a position to understand intimately the work of the British mineralogists of his time. Through his adherence to Werner's conception of descriptive geology, he played a prominent part in establishing petrography and mineralogy as independent branches of scientific research. Happy times when the rulers of states and their ministers had the leisure to enter seriously into such matters.

Investigating the details of Goethe's scientific activities we become

aware of the overwhelming breadth and depth of his interests. No part of the world was too remote, no detail of information too minute, to become to him a source of inspiration. The study of Goethe's relations with British scientists reveals his overruling sense of reality. While primarily interested in personal and philosophical aspects, he derived from these contacts an abundance of factual information, which he humbly accepted, digested, and assimilated. In many instances the emphasis which Goethe laid on, or the interpretation which he gave to, the various points in this information was far ahead of his time. His collection of minerals, still in their original arrangement, is preserved in the Goethehaus (now national Museum) at Weimar.

Summary.—As in other spheres of his scientific activities, in Goethe's mineralogical studies British scientists, notably Mawe, Macculoch, Greenough, and Scafe occupied a prominent place. From personal contacts with, and the reading of the works of these authors, Goethe derived detailed knowledge of the British mineralogy of his time and of the minerals of Britain, which were well represented in his collections.

References

Quotations given above (in my English translation) are taken from the Weimar edition of Goethe's collected works (133 vols., 1887–1919; including scientific works, 13 vols.). None of the references given below deals with Goethe's relations with British scientists.

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V. I. Vernadsky, Goethe comme naturaliste. Bull. Soc. Nat. Moscou, 1946, n. ser. vol. 51, Sect. Géol., vol. 21, no. 1, pp. 5–41 (Russian), pp. 41–52 (French résumé). [M.A. **10**–361.]

Gilbert Waterhouse, Goethe, Giesecke, and Dublin. Proc. Royal Irish Acad., 1933, vol. 41, sect. C, pp. 210–218; and Minutes of Proc. Royal Irish Acad., Session 1943 44, pp. 18–22. Goethe's relations with Sir Charles Giesecke, the German-born professor of mineralogy at the Royal Dublin Society, are outside the scope of the present paper. The 1933 paper gives a descriptive list of 63 specimens sent by Giesecke in June 1819 to Goethe. These include, besides Greenland minerals, several of Cornish cassiterite (crystals of various habits, and stream tin, from St. Agnes and St. Roach), also vivianite from Cornwall, wavellite from Devonshire, graphite from Borrowdale, and meteorite from Tipperary.

The occurrence of iron-cordierite in blast-furnace linings.[1]

By H. M. Richardson, B.Sc., and G. R. Rigby, Ph.D.
British Ceramic Research Association, Stoke-on-Trent.

[Read January 27, 1949.]

I. Introduction.

In an earlier paper[2] the authors described the occurrence of artificial kalsilite in the hearth of no. 3 blast-furnace of the Kettering Iron Company. That paper contained a detailed description of the furnace campaign together with the peculiar conditions observed in the excavated hearth which was found to exhibit zoning in a vertical direction. The third zone containing kalsilite was described in detail, but the only reference to the second zone stated that it was 2 inches deep (fig. 2, p. 77, this vol.) and consisted of a black glassy slag containing numerous crystals of cordierite (p. 78). The detailed examination of this zone now forms the basis of the present paper.

II. Examination of the black slag comprising zone 2.

Samples of this slag were examined by X-ray, petrological, and chemical methods. The percentage chemical analysis was: SiO_2 38·20, TiO_2 0·64, total iron as Fe_2O_3 27·07, Al_2O_3 32·89, CaO 0·59, MgO 0·68, K_2O 0·74, Na_2O 0·50. When examined under the microscope, thin sections of various samples from this zone were found to consist of numerous colourless crystals in a small amount of glassy matrix (fig. 1). The sizes of the crystals varied appreciably in different parts of the zone, but they were all square in cross-section as shown in figs. 1 and 2. They were biaxial negative, gave straight extinction, and polarized in first-order colours. The refractive indices of the crystals as determined by immersion of the powder were α 1·539 and γ 1·555. Certain crystals exhibited complicated twinning, as can be observed in fig. 2.

An X-ray powder photograph, using filtered cobalt radiation, gave a strong pattern closely resembling that given by artificially prepared

[1] Reprinted with slight alterations from Research Paper no. 14, 1948, British Ceramic Research Association.

[2] G. R. Rigby and H. M. Richardson, Min. Mag., 1947, vol. 28, p. 75.

cordierite, $2MgO.2Al_2O_3.5SiO_2$. The main strong reflections appeared to be almost identical with those of cordierite, but there were differences in spacing and intensity in some of the weaker reflections, as can be seen by comparing the data given in table I. The X-ray and petrological examinations also revealed the presence of small amounts of mullite and hercynite in some of the samples from this zone. Reference to the

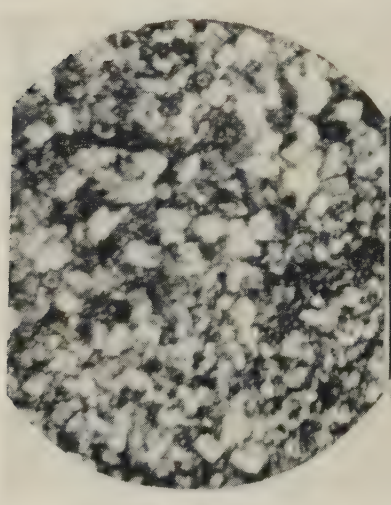

FIG. 1

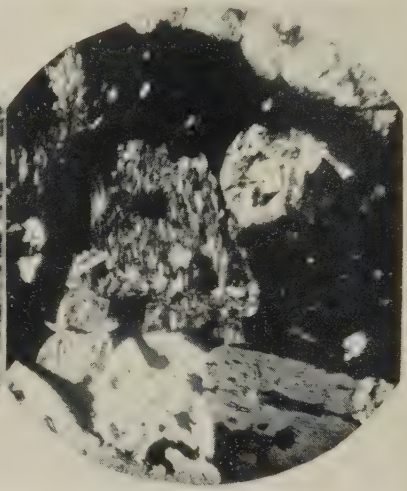

FIG. 2

FIG. 1. Thin section from the slagged material in zone 2, showing numerous colourless iron-cordierite crystals in a glass matrix. (Crossed nicols, × 100.)

FIG. 2. Larger iron-cordierite crystals from zone 2, exhibiting twinning. (Crossed nicols, × 100.)

chemical analysis clearly shows that these crystals, which formed the major phase in the samples from zone 2, could not be magnesium-cordierite as the magnesia content was very low (0·68%). On the other hand, the iron oxide content was quite high. The most probable assumption was that the crystals were those of a ferrous cordierite in which the magnesium ions in the structure of the mineral $2MgO.2Al_2O_3.5SiO_2$ were entirely replaced by ferrous irons.

Additional support was given to this hypothesis by the behaviour of the samples on oxidation. A sample of material was ground, magnetted to remove any metallic iron, and then heated in a stream of oxygen at 800° C. Under these conditions the sample gained 0·8% in weight, but X-ray powder photographs showed that an appreciable amount of iron-cordierite was still present. A second sample was then heated in oxygen

at 1200° C., when a gain in weight of 2·5% was finally obtained. X-ray examination showed that under these conditions the iron-cordierite had completely decomposed into ferric oxide, cristobalite, and mullite. A gain in weight of 2·5% is equivalent to the presence of 22·5% of ferrous iron in the original sample, so that the chemical analysis then approached very closely to that of $2FeO.2Al_2O_3.5SiO_2$. That the colourless crystals are composed of iron-cordierite is therefore placed beyond reasonable doubt, and table I lists the lattice reflections of this mineral together with those of the magnesium analogue to emphasize the close similarity between the powder photographs from the two minerals.

TABLE I. Lattice reflections of iron- and magnesium-cordierites.

Magnesium-cordierite		Iron-cordierite	
d (Å.)	Intensity.	*d* (Å.)	Intensity.
8·54	vs	8·54	vs
4·91	m	4·92	w
4·66	w	4·56	vw
4·09	s	4·06	s
3·37	s	3·43	s
3·13	s	3·13	fs
3·07	s	3·03	s
2·85	vw	2·85	vw
2·64	m	2·64	m
2·51	w	2·55	vw
2·42	m	2·45	m
2·34	m	2·31	m
2·28	vw		
2·23	w	2·23	vw
2·17	w	2·17	w
2·10	m	2·10	m
2·02	w	2·03	w
1·936	mw	1·954	mw
1·872	m	1·877	m
1·853	vw	1·858	vw
1·798	m	1·790	m
		1·718	w
1·685	fs	1·685	fs
1·650	w	1·658	vw
1·588	m	1·594	w
1·488	m	1·497	w
		1·473	w
1·457	w	1·451	w
1·444	w	1·415	vw
1·398	w	1·389	w
		1·368	w
1·348	m	1·353	m
		1·330	w
1·315	m	1·310	w
1·296	w	1·295	vw

III. Earlier references to iron-cordierite.

In 1900 H. Bücking[1] investigated a few black fragments resembling obsidian in appearance associated with ejected blocks of andesite from the volcano Seputan in north Celebes. Under the microscope they consisted of minute crystals of fresh cordierite with a very little glass and associated with magnetite (about 4%) and either augite or sillimanite. The percentage analysis was as follows: SiO_2 49·15, Al_2O_3 31·84, Fe_2O_3 2·88, FeO 11·49, CaO 4·30, MgO 0·55, loss on ignition 0·06. He gave the name *Kalkeisencordierit* to this mineral; and that of *Eisencordierit* to similar (unanalysed) material in 'vitrified' Bunter sandstone in contact with basalt in central Germany. It is interesting to note that if Bücking's sillimanite mineral was in reality mullite, his natural product bears a close resemblance to the material found in the blast-furnace hearth.

L. L. Fermor[2] in 1923 applied the name *iron-cordierite* to a violet-coloured cordierite rich in ferrous oxide and almost devoid of magnesia occurring in shale that had been fused by burning coal-seams in India. Analyses of cordierite listed by Dana (System, 6th edit., 1892, p. 420) show various amounts of ferrous oxide up to a maximum of 9·24%. In 1936 H. Shibata[3] described iron-rich cordierites (FeO 15·31, MgO 1·48 and FeO 13·17, MgO 2·70%) from Japan, occurring in pegmatites intrusive into and contaminated by sandstone and amphibolite.

E. Dittler and A. Köhler[4] were unsuccessful in their attempts to prepare pure iron-cordierite by heating the oxides at 1000-1400° C., as the products of reaction contained magnetite, spinel, and sillimanite. They claimed, however, to have prepared small optically negative crystals of the general composition $2(Mg,Fe)O.2Al_2O_3.5SiO_2$. These mixed crystals contained 25, 50, and 75% of iron-cordierite in their composition.

The FeO–Al_2O_3–SiO_2, ternary phase-rule diagram as far as it has been determined, has no provision for any ternary compounds,[5] although the corresponding ternary diagram MnO–Al_2O_3–SiO_2 includes fields of stability of two ternary compounds, a spessartine garnet, $3MnO.Al_2O_3.3SiO_2$, and

[1] H. Bücking, Ber. Senckenberg. Naturfor. Gesell. Frankfurt am Main, 1900, p. 3. [Min. Mag. 1903, vol. 13, pp. 367, 369.]

[2] L. L. Fermor, Abstr. Proc. Geol. Soc. London, 1923, for 1922–23, p. 96; Quart. Journ. Geol. Soc. London, 1924, vol. 80, p. 70. [Min. Mag., 1924–25, vol. 20, pp. 250, 456.]

[3] H. Shibata, Japanese Journ. Geol. Geogr., 1936, vol. 13, p. 205. [M.A. **6**–479.]

[4] E. Dittler and A. Köhler, Zentralbl. Min., Abt. A, 1938, p. 149. [M.A. **7**–283.]

[5] J. F. Schairer, Journ. Amer. Ceram. Soc., 1942, vol. 25, p. 245. [M.A. **9**–16.]

a manganese-cordierite, $2MnO.2Al_2O_3.5SiO_2$.[1] The latter mineral has the following reported optical properties; uniaxial or biaxial negative with a small axial angle, refractive indices α 1·537, γ 1·558. In addition, a manganese analogue of anorthite has been stated by J. R. Rait and H. W. Pinder[2] to occur in inclusions in steel. The garnet almandine, $3FeO.Al_2O_3.3SiO_2$, has been reported from time to time as occuring in slags,[3] but confirmatory evidence is lacking, so that iron-cordierite must be considered as the only ternary compound of FeO, Al_2O_3, and SiO_2 to occur artificially.

IV. Attempts to synthesize iron-cordierite in the laboratory.

Since iron-cordierite has been detected in the blast-furnace it might be thought that synthesis of it in the laboratory would present no unusual difficulties. Contrary to expectations, however, it has been found most difficult to prepare and the best of the laboratory samples falls far short of those obtained in the furnace hearth.

Preliminary experiments have already been described in which it was shown that the hearth sample of iron-cordierite on oxidation was decomposed to ferric oxide, cristobalite, and mullite, accompanied by a gain in weight of 2·5%. At 800° C. the oxidation was very slow, and when heated in air over a Méker burner the gain in weight remained constant at 0·9%, but the material after this treatment still contained a high percentage of iron-cordierite together with some ferric oxide. The blast-furnace sample therefore appeared fairly resistant to oxidation, the crystals of iron-cordierite probably being protected by the glass matrix.

The refractoriness of a cone cut from the glassy layer was 1200° C. in an atmosphere of nitrogen. The deformed cone contained iron-cordierite along with a spinel solid solution, thereby indicating that the mineral was slowly decomposing at 1200° C. into hercynite, magnetite, and a siliceous glass. More extended experiments fixed the upper temperature limit of stability at below 1100° C., while at 1400° C. decomposition into hercynite, mullite, and magnetite was complete after 2 hours. The presence of metallic iron did not appreciably increase the stability range, as decomposition still occurred at 1200° C.

The glassy nature of the layer indicated that iron-cordierite had crystallized out from a glass. This suggested that at one period in the furnace campaign the hearth of zone 2 must have contained a considerable

[1] R. B. Snow, ibid., 1943, vol. 26, p. 15. [M.A. **10**–461.]

[2] J. R. Rait and H. W. Pinder, Journ. Iron and Steel Inst., 1947, vol. 154 (no. 2 for 1946), p. 371P. [M.A. **10** 462.]

[3] H. E. Simpson, Journ. Amer. Ceram. Soc., 1932, vol. 15, p. 520.

amount of liquid on account of the temperature of this zone being around or above 1200° C. At a later stage the temperature of zone 2 must have dropped below 1100° C. to allow the crystallization of iron-cordierite, the temperature possibly remaining at this lower level for a considerable period. The instability of iron-cordierite above 1100° C. provides a ready explanation of its absences from the ternary FeO–Al_2O_3–SiO_2 diagram. It has also been shown that when firebricks are attacked by ferrous oxide, hercynite and fayalite are generally found in the products of reaction.[1]

Attempts were next made to induce ferrous oxide to react with firebrick and china-clay at a low temperature. No reaction could be detected below 900° C., but even at this temperature the first product of the reaction was hercynite and not iron-cordierite, and the presence of various fluxes, metallic iron, or carbon did not alter the trend of the reaction, as in all cases hercynite and fayalite were formed and no iron-cordierite could be detected. It was next thought that iron-cordierite might be induced to form in the presence of magnesium-cordierite. Mixtures of ferrous oxide and magnesium-cordierite ranging from 5 to 50 % of FeO were heated together at temperatures varying between 800° and 1200° C. No reaction took place below 900° C., but at higher temperatures the cordierite was decomposed to hercynite and fayalite, and X-ray photographs gave no evidence of the formation of mixed crystals of magnesium- and iron-cordierite due to replacement of magnesium by ferrous ions. Further experiments in which mixtures of firebrick or china-clay with metallic iron or mixtures of metallic iron and ferrous oxide were heated in nitrogen and steam for prolonged periods at 1080° C. proved equally abortive, as the reaction products always included hercynite, fayalite, mullite, cristobalite, magnetite, or ferric oxide, with no trace of iron-cordierite. The application of external pressure to the mixture or the introduction of small amounts of magnesium-cordierite had no influence on the course of the reactions.

Partial success was at last achieved by one method alone. A mixture of ferrous oxide, alumina, and hydrated silica in the correct molecular proportions for iron-cordierite was prepared, and to this was added 5 % of potassium carbonate. The potash addition facilitated melting and the formation of a glass, for on heating in an iron tube to 1480° C. in nitrogen following by quenching, a glass was obtained which only contained a trace of undissolved corundum and hercynite.

[1] H. M. Richardson, F. Ball, and G. R. Rigby, Gas Research Board, 38th Report of the Refractory Materials Joint Committee, 1946–47, p. 38.

A sample of this glass was then held at various temperatures between 800° and 1100° C. in an atmosphere of nitrogen for periods of up to 200 hours. After being heated for 120 hours at 850° C. iron-cordierite had crystallized out, but the maximum amount was obtained after heating the glass at 900° C. for about 100 hours. This iron-cordierite was always accompanied by other crystalline phases such as hercynite, fayalite, and pyroxene, and, if the temperature of crystallization rose to 1000° C. or higher, the relative proportions of iron-cordierite decreased in favour of the hercynite phase.

These experiments, while not being as conclusive as one could wish, have clearly shown, however, that iron-cordierite can be formed by inducing certain glasses to crystallize over the temperature range 850 - 1000° C. It is considered that the mechanism by which iron-cordierite was synthesized in the blast-furnace hearth followed a similar procedure.

V. The presence of iron-cordierite in refractory materials.

Since the detection of iron-cordierite in samples from the Kettering blast-furnace hearth, this mineral has been identified in vitrified bricks taken from the hearths of four other furnaces, although the amounts present were very much smaller than those in the Kettering samples.

It has also been found to occur in the black cores associated with certain fireclay casting-pit refractories. In a thin section, minute crystals of iron-cordierite can be readily detected in the fringes of pores present in the darkest areas of the black core. Traces of iron-cordierite have also been noticed associated with glassy iron spots in various types of firebricks. Indeed, it is possible that the mineral is found in a wide range of refractory products, though nearly always in very small amounts and then only in isolated areas within the refractory. The material has also been observed in various refractory materials by K. W. Andrews and J. Mackenzie of the United Steel Companies, Ltd., and their findings are given in the appendix to this paper.

VI. The reversible thermal expansion of iron-cordierite.

Particular interest attaches to the thermal expansion of iron-cordierite since it is well known that the corresponding expansion of the magnesium analogue is very small, the coefficient being only about $2{\cdot}3 \times 10^{-6}$ between 100° and 1000° C.[1] With the samples available it was found impossible to free the iron-cordierite crystals from the glass, and accordingly a suitable specimen for a thermal expansion determination was cut from the

[1] G. R. Rigby and A. T. Green, Trans. Brit. Ceram. Soc., 1942, vol. 41, p. 123.

glassy material of zone 2. The reversible thermal expansion data are given in table II, where they are compared with similar data obtained earlier for magnesium-cordierite. It must be remembered, however, that unlike the magnesium-cordierite, the sample of iron-cordierite was contaminated with a little glass, mullite, hercynite, and metallic iron, all of which would tend to increase the reversible expansion, the figures reported in table II being too high. The results clearly show that iron-cordierite has a remarkably low coefficient of expansion, being well below that of mullite or the ferrous silicates generally. It has been found earlier that the substitution of magnesium ions for ferrous ions, in the case of the olivine minerals, results in a slight increase in the expansion coefficient.[1] It may well be, therefore, that if a pure specimen of iron-cordierite could be prepared, the thermal expansion would be as low or even lower than that of magnesium-cordierite.

TABLE II. The thermal expansion characteristics of magnesium- and iron-cordierite.

	Percentage thermal expansion and coefficient of expansion $\times 10^6$ between 100° C. and						
	200°	300°	400°	500°	600°	700°	800° C.
Magnesium-cordierite	0·006	0·020	0·034	0·057	0·081	0·110	0·139
	0·6	1·0	1·2	1·4	1·6	1·7	1·9
Iron-cordierite ...	0·02	0·048	0·075	0·103	0·130	0·158	0·185
	2·0	2·4	2·5	2·6	2·6	2·6	2·7

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APPENDIX

By K. W. ANDREWS, D.Phil., and J. MACKENZIE, B.Sc.

The United Steel Companies, Ltd., Research and Development Dept., Stocksbridge, near Sheffield.

The presence of a cordierite-type mineral, similar to that described by H. M. Richardson and G. R. Rigby as iron-cordierite, has been confirmed in samples taken from the break-out area of a blast-furnace hearth and the black core of certain fireclay casting-pit refractories.

[1] G. R. Rigby, G. H. B. Lovell, and A. T. Green, Trans. Brit. Ceram. Soc., 1946, vol. 45, p. 237.

The results of an examination of the break-out area of the fireclay hearth of no. 6 furnace, Appleby-Frodingham, have been reported elsewhere.[1]

The typical zoned deterioration of the brickwork was noted at the time, i.e. the almost unchanged metal-free brickwork on the casing side changing to the metal-bearing FeO reduction zone and slagged zones on the metal side. Samples of these individual zones were examined by the X-ray powder method, the mineralogical constitution together with chemical composition being shown in table III.

The cordierite-type compound has spacings near to those given by Richardson and Rigby, but the agreement is not exact and the presence of some MgO or even other oxides is suggested.

The existence of this iron-cordierite mineral therefore confirms constitutionally the presence of a ferrous iron compound in the blast-furnace hearth resulting from the slagging of the alumino-silicate refractory by the oxidized metal in the pores of the brick.

Certain fireclay casting-pit refractories, which contain a black core, were examined by X-rays with the following results:—

Guide tube I—

(*a*) Clear portion: mullite, large amount; quartz, small to medium.

(*b*) Black core: mullite, large amount; quartz, medium to small; iron-cordierite, very small to small.

Guide tube II—

(*b*) Black core: mullite, large amount; quartz, small to very small; iron-cordierite, medium to small; cristobalite, possible, small.

TABLE III.

Sample.	Chemical analysis. SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	MnO.	Mineralogical constitution and amount.
Outer zone (casing side), mauve-coloured brickwork	58·3	33·8	0·76	2·78	0·69	0·01	Mullite, medium to large. Cristobalite, medium.
White zone	58·4	33·5	0·84	2·85	0·78	—	Mullite, medium to large. Cristobalite, medium. Iron-cordierite, small.

[1] G. D. Elliot and collaborators, Iron and Steel Inst., 1944, Spec. Rep. no. 30, p. 262.

TABLE III (*cont.*)

Sample.	Chemical analysis. SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	MnO.	Mineralogical constitution and amount.
FeO reduction zone, slagged	48·65	27·39	4·31	13·35	0·69	—	Mullite, small. Cristobalite, small. Iron-cordierite, large. Metallic iron.*
Inner zone (metal side), slagged.	56·35	31·96	0·28	2·93	0·69	3·89	Mullite, medium to large. Cristobalite, medium. Iron-cordierite, small. Metallic iron.*

*Metallic iron was removed by a magnet.

The cordierite compound had lattice spacings near to those given for iron-cordierite, but again a small amount of solid solution is possible.

The presence of a cordierite-type compound in the black core was also suggested by petrological examination, but in such small amounts this was difficult to identify with certainty. A magnetic separation was carried out and it was found that the very small amount of iron-cordierite tended to concentrate in the magnetic fraction. It is not suggested that iron-cordierite is itself magnetic, but it would appear to be associated with the magnetic iron material present in the fireclay brick.

The authors of the appendix wish to thank Mr. F. H. Saniter, Director of Research, United Steel Companies, Ltd., for permission to publish this information, and Dr. W. Davies for his assistance in petrological examinations.

Crystallization of basaltic magma as recorded by variation of crystal-size in dikes.

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[Taken as read November 25, 1948.]

IT is a familiar fact that in dikes, lava-flows, and sills the grain-size of the individual minerals normally varies according to the distance from the contacts. At or near the margins of the igneous body the grain-size is usually very much less than in the centre, and this phenomenon has been attributed to differences in the cooling-velocities at these spots. On the basis of measurements carried out by Queneau (8) the opinion seems to have been formed that the crystal-size always shows a progressive increase from the contacts towards the centre. This is not so, however, for as Lane (6) has shown, the crystal-size may increase to a maximum at a certain distance from the margin, and thereafter decrease again towards the centre of the intrusion. Apart from these investigations, carried out by Queneau and Lane, the only additional quantitative data on crystal-size variation known to the writer concerns a series of measurements made on an olivine-diabase by B. H. Dollen, under the direction of H. L. Alling (1).

The crystal-size variations in the three dikes (minette, quartz-diabase, and olivine-diabase) measured by the authors cited have recently been interpreted by the writer (12) on the basis of:

(*a*) calculated cooling-velocities for various temperature ranges at different distances from the contact;
(*b*) experimental work on the relationship between cooling-velocity and crystal-size.

From these the relationship between distance from the contact and crystal-size can be derived. It has been shown, moreover, that the curves representing the relationship between grain-size variation and distance from the walls for various minerals also give an indication of the temperature ranges throughout which the individual minerals have crystallized in a magma (11) (12).

The present paper deals with the application of these principles to the Cleveland dike, a representative of the tholeiitic magma-type,

which can be traced from Yorkshire to the island of Cumbrae, in the Firth of Clyde, throughout a distance of 310 km. Mull constitutes the intrusion centre, and the dike thus has a total length of about 400 km. Before dealing with this intrusion, however, it is necessary to outline briefly the principles employed in the interpretation of crystal-size variations in dikes (12).

Relationship between cooling-velocity and distance from the cooling-wall.

A dike intruded into colder country-rock can be regarded as a plate of a certain thickness subjected to cooling. In a vertical dike cooling

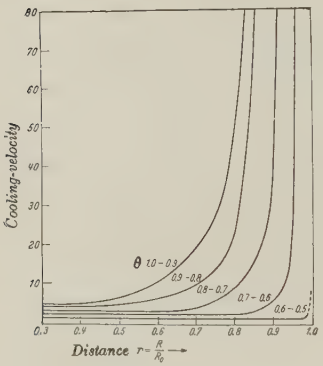

Fig. 1.

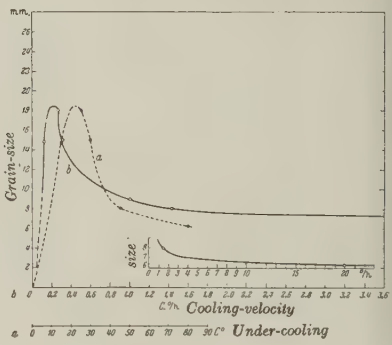

Fig. 2.

Fig. 1. Relationship between cooling-velocity and distance from the margin in a dike for various temperature ranges (θ-values).

Fig. 2. Relationship between crystal-size and (a) under-cooling and (b) cooling-velocity.

will be symmetrical with respect to both walls, so that only one-half of the intrusion, from margin to centre, need be considered. If we assume that the conductivity of heat is the same in the magmatic body as in the country-rock, and omit complications due to convective currents, then it is possible to calculate mathematically the cooling-velocity at different distances from the margin. This has been done for various temperature ranges, using the following data:

Specific gravity = 2·9,
Conductivity of heat = 0·006 cal. cm.$^{-1}$ sec.$^{-1}$ centigrade^{-1},
Specific heat = 0·2 cal. g.$^{-1}$ centigrade^{-1}.

The results for various temperature ranges are given in table I and partly in fig. 1. They refer to a dike of a thickness of 2 metres, i.e. half thickness $R_0 = 1$ m. Since cooling-velocity is reciprocal to the

square of the thickness, the given values are to be multiplied by a certain factor if thicknesses other than $R_0 = 1$ m. are to be dealt with.

For a dike of $R_0 = 2$ m. this factor is 1/4
„ „ $R_0 = 3$ m. „ „ 1/9
„ „ $R_0 = 4$ m. „ „ 1/16, &c.

It is impossible to account accurately for the liberated heat of crystallization. If it is assumed that during crystallization of the main constituents heat is almost evenly liberated, then the given values for cooling-velocity will become smaller by a constant factor (Lovering (7)). Thus the ratio of cooling-velocities which actually suffice to explain our observations concerning crystal-size variation will not be affected, and this factor need not be considered.

TABLE I. Mean cooling-velocities in °C./h prevailing in indicated temperature ranges. Infinite plate of half thickness $R_0 = 1$ m.

	θ-values.								
r	1·0–0·9.	0·95–0·85.	0·90–0·80.	0·85–0·75.	0·80–0·70.	0·75–0·65.	0·70–0·60.	0·65–0·55.	0·60–0·50.
0·95	—	—	320	300	165	120	28	6·24	1·08
0·90	180	160	149	100	50	16·6	6·0	2·02	0·99
0·85	108	83	72	29	15·4	7·6	3·3	1·52	0·99
0·80	53	37	22·5	14	8·3	4·4	2·09	1·48	0·99
0·75	31	21·5	14·5	9·5	5·4	3·2	2·06	1·44	0·99
0·70	20·5	15·0	10·4	6·3	4·0	2·6	2·03	1·40	0·99
0·65	14·8	11·0	7·3	4·9	3·5	2·50	2·00	1·35	0·99
0·60	11·2	8·0	6·1	4·1	3·0	2·47	1·98	1·35	0·99
0·55	8·5	6·2	5·2	3·8	3·0	2·44	1·98	1·35	0·99
0·50	6·5	5·4	4·8	3·6	3·0	2·41	1·98	1·35	0·99
0·45	5·7	4·8	4·3	3·6	2·9	2·39	1·98	1·35	0·99
0·40	4·8	4·6	4·1	3·6	2·9	2·37	1·98	1·35	0·99
0·30	4·7	4·5	4·0	3·6	2·9	2·37	1·98	1·35	0·99
0·20	4·6	4·4	4·0	3·6	2·8	2·37	1·98	1·35	0·99
0·10	4·5	4·3	4·0	3·6	2·8	2·37	1·98	1·25	0·99
0·00	4·5	4·3	4·0	3·6	2·8	2·37	1·98	1·35	0·99

r	0·90–0·70.	0·85–0·65.	0·80–0·60.	0·75–0·55.	0·70–0·50.
0·95	305	180	56	14	2·15
0·90	59	32·6	10·8	3·64	1·74
0·85	24·5	12·2	5·4	2·40	1·58
0·80	12·4	6·7	3·5	2·07	1·52
0·75	7·6	4·8	2·8	1·98	1·52
0·70	5·80	3·7	2·56	1·90	1·52
0·65	4·75	3·15	2·44	1·89	1·52
0·60	4·09	3·05	2·35	1·89	1·52
0·55	3·69	3·00	2·35	1·89	1·52
0·50	3·57	2·95	2·35	1·89	1·52

TABLE I (*cont.*)

r	0·90–0·70.	0·85–0·65.	0·80–0·60.	0·75–0·55.	0·70–0·50.
0·45	3·44	2·91	2·35	1·89	1·52
0·40	3·37	2·88	2·35	1·89	1·52
0·30	3·37	2·85	2·35	1·89	1·52
0·20	3·37	2·85	2·35	1·89	1·52
0·10	3·37	2·85	2·35	1·89	1·52
0·00	3·37	2·85	2·35	1·89	1·52

r	0·90–0·75.	0·85–0·70.	0·80–0·65.	0·75–0·60.	0·70–0·55.
0·95	—	280	114	44	9·2
0·90	114	65	25	8·6	2·8
0·85	35	20	9·5	4·37	1·91
0·80	18·3	9·4	5·7	2·77	1·70
0·75	10·4	6·45	3·77	2·28	1·58
0·70	7·2	5·09	3·05	2·23	1·56
0·65	5·8	4·05	2·78	2·19	1·56
0·60	5·0	3·55	2·68	2·19	1·56
0·55	4·2	3·42	2·60	2·19	1·56
0·50	4·06	3·33	2·60	2·19	1·56
0·45	3·79	3·24	2·60	2·19	1·56
0·40	3·78	3·15	2·60	2·19	1·56
0·30	3·78	3·15	2·60	2·19	1·56
0·20	3·78	3·15	2·60	2·19	1·56
0·10	3·78	3·15	2·60	2·19	1·56
0·00	3·78	3·15	2·60	2·19	1·56

Fig. 1 shows the cooling-velocity at different distances from an igneous contact. The abscissa represents distance in terms of $r = R/R_0$, in order to facilitate comparison in dikes of various thicknesses. R is the distance from the centre of a dike to a point in the cross-section, and R_0 the distance from the centre to the margin. Thus $r = 0{\cdot}0$ is the centre and $r = 1{\cdot}0$ the margin. (For example, assuming a dike of total thickness 6 m. then $R_3 = 3$ m. A specimen taken at a distance of 2·1 m. from the centre (in the cross-section) equals $R = 2{\cdot}1$ m.; $r = 2 \times 1/3 = 0{\cdot}7$.) The ordinate gives the cooling-velocities in °C./h. At constant distance the cooling-velocity diminishes continuously with progressive cooling of the body, but for our purpose successive steps of temperature ranges have been chosen for which the *mean* cooling-velocity is given. These temperature ranges are designated by θ-values. $\theta = (T - T_c)/(T_m - T_c)$, where T_c is the temperature of the country-rock immediately before intrusion, T_m is the temperature of the magma immediately after intrusion, and T is the temperature deriving from θ, T_c and T_m. Assuming, for simplicity, $T_m = 1000°$ C. and $T_c = 0°$ C., then θ 1·0–0·9 indicates the temperature range from 1000° to 900° C.,

θ 0·9–0·8 900°–800°, &c. The curves in fig. 1 and the values in table I represent the mean values of the cooling-velocity in the designated temperature ranges at different distances from the centre of the dike.

Relationship between cooling-velocity and crystal-size.

The interpretation of variation in crystal-size at different distances from the centre of a dike depends on (*a*) the relationship between cooling-velocity and distance from the centre, and (*b*) the relationship between cooling-velocity and crystal-size. When these two relationships are known, curves can be constructed to show the variation of crystal-size with distance.

The mean of the maximum crystal-size (that is, the mean size of the crystals when crystallization is completed) has been determined experimentally for various degrees of under-cooling (11). A silicate melt was used from which the rock-forming mineral nepheline crystallized. The size is given as the mean diameter of the crystals measured from one prism face to the opposite one. The crystal-size itself depends on two factors: (*a*) the rate of formation of crystal nuclei, and (*b*) the velocity of growth. Both have been experimentally determined for different degrees of under-cooling and the quantitative relationship between these two primary factors has been worked out. The crystal-size equals

$$\text{Constant} \times \sqrt[4]{(\text{velocity of growth/rate of formation of nuclei})}.$$

For the present purpose, however, these two primary factors governing crystal-size need no longer be dealt with (cf. (11)). Velocity of growth and rate of formation of nuclei vary with under-cooling, and therefore crystal-size varies with it also. This is shown in fig. 2 by curve *a*, broken line. As under-cooling decreases crystal-size increases up to a maximum and then falls to the zero-point of the co-ordinate system, at which point no crystals form.

There is obviously a close connexion between under-cooling and cooling-velocity, for similar effects are produced by a marked degree of under-cooling on the one hand and high cooling-velocity on the other. In both cases small crystals develop. This connexion has been worked out and it is possible to correlate crystal-size, developed at a certain degree of under-cooling, with a certain cooling-velocity (11) (12). The result is shown in fig. 2, curve *b*, full line. It should be noted that with decrease in cooling-velocity there is merely a small increase in crystal-size over a wide range until certain low cooling-velocities are approached,

when rapid increase takes place. At very low cooling-velocities there is a rapid decrease in crystal-size. This fact has not previously been observed, but is experimentally and thermodynamically well founded, and is of great significance in the interpretation of the phenomena observed in nature. (Discussion of Queneau's and Lane's conceptions (in 12).)

Relationship between crystal-size and distance from margin.

Although the actual values given in fig. 2 refer only to nepheline crystallized in a certain system, it can reasonably be assumed that the same relationship between crystal-size and cooling-velocity, as represented by curve *b*, will hold for other rock-forming minerals. This assumption is supported by the agreement between the observed and calculated curves expressing the relationship between crystal-size and distance from the centre in dikes. Such curves, based on the outlined relationship between (*a*) cooling-velocity and distance from the centre, and (*b*) cooling-velocity and crystal-size, have been constructed for dikes of various thicknesses (12). The results for dikes of $R_0 = 1$ m., 2 m., 3 m., 4 m., 5 m., and 6 m., all belonging to the same magma and having the same viscosity, are here again produced as graphs. These have been constructed as follows. Assuming a dike of $R_0 = 3$ m., and regarding the temperature range of θ 1·0–0·9, the cooling-velocity at a distance of $r = 0{\cdot}7$ (corresponding to the distance of 2·1 m. from the centre) is obtained from table I; it is 20·5 °C./*h* multiplied by 1/9 = 2·28 °C./*h*. From fig. 2, curve *b*, it is found that the crystal-size of 7·5 mm. diameter corresponds to this cooling-velocity. This value is plotted at the distance $r = 0{\cdot}7$ in fig. 5. When similarly derived values for other distances are plotted, a curve is obtained which shows the variation of crystal-size with distance for the case of a mineral crystallized within the temperature range of θ 1·0–0·9. The same procedure is carried out for other temperature ranges indicated on the corresponding curves in the diagrams. (Figs. 3–8 represent various thicknesses.)

Having regard to the diagrams for various thicknesses it is noticed that in thin dikes ($R_0 = 1$ m.; fig. 3) hardly any change in crystal-size takes place; this has often been observed in nature. In thicker dikes ($R_0 = 2$ m.; fig. 4) the crystals become larger with increasing distance from the margin, and maintain the maximum value in the central portion of the dike. If still thicker dikes are considered, however, crystals which have grown within certain temperature ranges no longer attain a maximum size at the centre of the dike, but show a pronounced maximum

at a certain (intermediate) distance from the margin. This has been observed by Lane (6) in the Medford dike at Cambridge, Massachusetts, and has been interpreted by the writer (12).

When the temperature of the intrusion has fallen to half or less than half of its original value (T_m) no differences in cooling-velocity exist across the dike, and hence there is no variation in crystal-size.

Grain-size measurements carried out on naturally occurring dikes can be interpreted on the basis of the data incorporated in the constructed curves, and afford valuable information concerning the temperature ranges within which individual minerals have grown, and even provide some indication of the viscosity of the various magmas (12). There is one point which must be stressed, however, viz. that in speaking of temperature ranges in which various minerals have crystallized, it is not implied that, quantitatively, all of a mineral has crystallized within a certain range of temperature, but that by far the greater quantity did so. It is not possible to be more precise (except in individual cases, as we shall see below, page 571, as the method employed is based on the determination of the mean diameter of a great number of crystals. If, for instance, after the bulk of a mineral has crystallized in a certain temperature range a further 15% crystallizes out later, this will often not influence to any extent the crystal-size of the earlier formed 85%. This should be born in mind when comparing the results of crystal-size interpretation which lead to the deduction of crystallization ranges with those derived from the study of ternary and quaternary systems (see p. 570).

In the following pages new measurements of grain-size in a tholeiite dike are given and interpreted.

Crystal-size variation in the Cleveland dike.

The rock.—One of the localities which afford a complete section of the Cleveland dike, from one margin to the other, is Great Ayton, south of Middlesborough, in Yorkshire. The dike is there exposed in underground workings, and is seen to be almost vertical and with a total thickness of 54·5 feet, or 16·6 m. Specimens have been taken from one margin to the other at intervals normally of 1·5 feet except in the central parts of the dike (15–42 feet from the south margin) where the distance between successive specimens was increased to 3 feet. The orientation of all specimens was marked, and thin sections were cut in such a way that the plane of the section is horizontal and perpendicular to the walls of the intrusion.

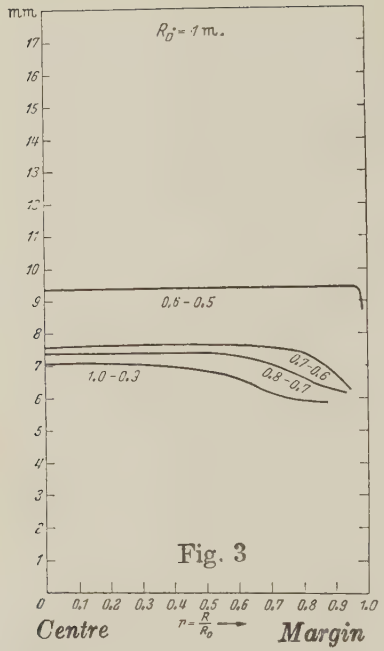

Fig. 3

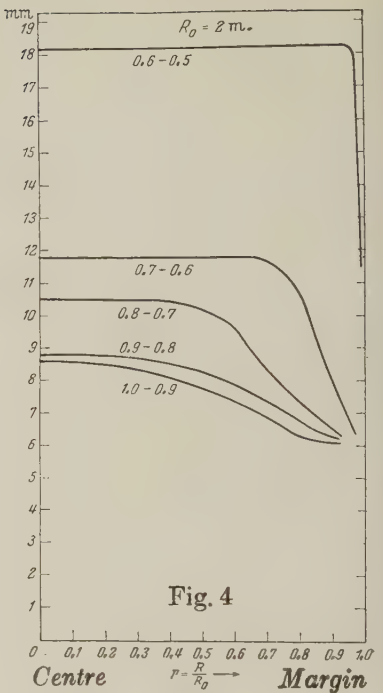

Fig. 4

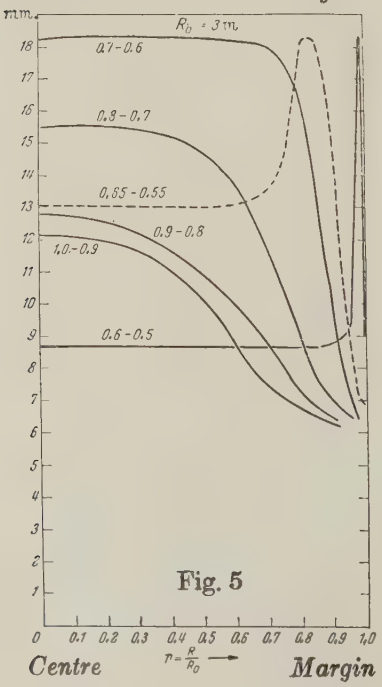

Fig. 5

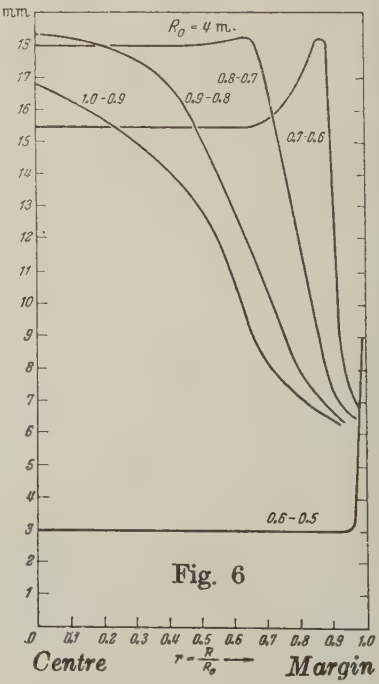

Fig. 6

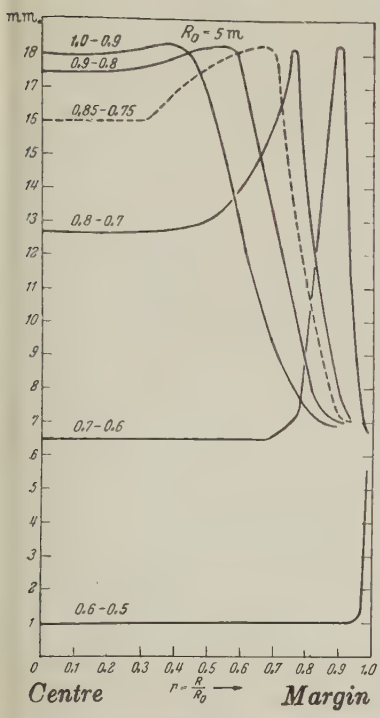

Fig. 7

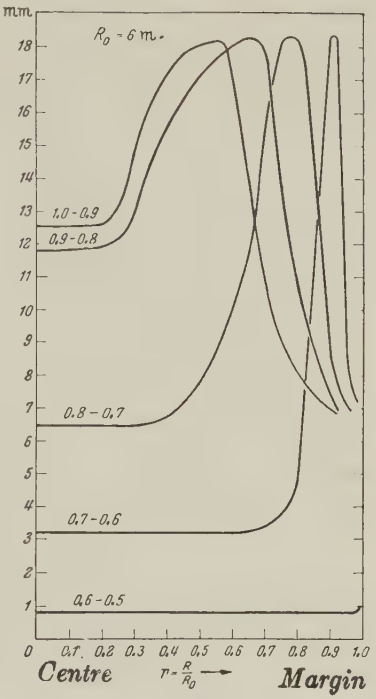

Fig. 8

FIGS. 3–8. Crystal-size variation in dikes from the centre to the margin for various temperature ranges and thicknesses (R_0 being half of the total thickness).

The rock of the Cleveland dike has previously been fully described by J. J. H. Teall (9) and A. Holmes (4). It is a typical tholeiite characterized by basaltic composition and the development of intersertal texture. A very fine-grained variety near the margin is always distinct from the coarser-grained rock of the main mass, but apart from this no further variation in grain-size can be detected in the hand-specimens. Typically porphyritic crystals of plagioclase, ranging in size up to 2×4 mm., are as well developed, and of the same size, at and near the margins as in the centre of the dike. These constitute on an average 3 or 4% of the rock. Very subordinately scattered porphyritic crystals of enstatite-augite are also distributed throughout the rock. The groundmass is made up of plagioclase laths ranging in composition from labradorite to oligoclase, and with only slight zoning. The interstices are occupied by augite, magnetite, very little quartz, biotite, and much

mesostasis. The latter is devitrified, and comprises about 30–40 vol. % of the rock. Magnetite is evenly distributed as idiomorphic and sometimes as skeleton forms, and the augite occurs as grains and slender prisms.

Although the texture must be described as intersertal there are some exceptions from the point of view of an ideal intersertal texture, in that magnetite and, more often, pyroxene crystals are occasionally partly intergrown with the felspar laths of the groundmass. This indicates that crystallization of some plagioclase took place after some individual crystals of magnetite and augite had already developed. This observation will be discussed further, below.

Measuring of crystal-sizes. A number of methods have been used in the measurement of the diameters of crystals in thin sections. Some of these have been described by H. L. Alling (1), who himself uses, for accurate work, a camera-lucida and polar-planimeter equipment, with which the area of fifty grains of each mineral in each slide is measured. From the mean area of all grains measured the diameter of a circle equal to this area is calculated, and this is taken as the mean diameter of the crystals. In the present investigation the writer used an integrating stage, and, as the crystals are randomly distributed, measured 350 to 400 crystals of each mineral in each slide. The total sum of diameters divided by the number of crystals gives the mean diameter.

In the specimens taken from the margin of the dike and at a distance of 1·5 feet inwards the plagioclase laths of the groundmass tend to be orientated with their longer axis almost perpendicular to the cooling-wall. (This is a growth effect due to the great heat transport and consequently molecule diffusion towards the wall.) In these cases the section was measured in two directions, one perpendicular to the other, and the mean value determined from both sets of measurements. It would appear, moreover, that in addition to this orientation there is still another orientation effect, in which the two longest axes of the felspar laths lie more or less in a horizontal plane (floating effect). This is also the plane of the slides. Thus the mean crystal-size of plagioclases measured in these two sections is not the true mean diameter, but is too great. This may explain the observation that the two values at and close to the margin do not fit the general trend of the curve, which is accurately determined by the other points (see broken line in fig. 9).

As shown by the calculated curves, conspicuous changes in crystal-size must be expected especially at distances extending from the margins inwards up to about one quarter of the total thickness of the dike.

Specimens have therefore been taken at closer intervals in these marginal parts than in the middle portion of the dike. This is essential in order to obtain an accurate curve of crystal-size variation. It would be advisable to choose even smaller intervals, because all specimens taken represent chance sections and may depart to some extent from the true mean value. This, however, can be interpolated graphically if enough points are available for the graph.

In the present instance 27 specimens have been taken across the whole dike, but since the northern part of the cross-section (extending 12·5 feet from the north margin into the dike) contained mainly decomposed augites which could not always be distinguished individually, only the southern half of the dike, involving 15 thin sections, has been investigated.

Results of measurements.—The results of the measurements are plotted in fig. 9. The abscissa represents the distance from the margin to the centre of the dike. The ordinate gives the mean diameter of the crystals in millimetres. Since the graph would have become too long the curves for augite and magnetite have been displaced upwards; and the ordinate on the right-hand side refers to these two minerals, while the left ordinate refers to plagioclase. Only the three minerals of the groundmass are considered, the porphyritic crystals of intratelluric origin being ignored.

As the specimens have been taken at rather small intervals, the curves which link up the individual values represent crystal-size variation with a comparatively high degree of accuracy, and so a reliable interpretation is possible. It is noticed from fig. 9 that the curves for plagioclase, augite, and magnetite are very different in character. Proceeding from the margin to the centre, the plagioclase curve rises steeply to a maximum and thereafter remains constant, whereas the magnetite and, more conspicuously, the augite curves show a definite size maximum followed by a decrease at a certain distance from the margin.

Interpretation of crystal-size variation in the tholeiite dike.

The observed crystal-size variation of the minerals plagioclase, augite, and magnetite can be compared with curves constructed independently by methods based on the principles responsible for the variation of crystal-size in dikes. In so doing, merely the character of the curves has to be compared, disregarding the absolute crystal-size. Furthermore, the three curves for plagioclase, augite, and magnetite, as determined in the dike, must all be represented in one of the constructed diagrams.

If the curves of fig. 9 are compared in this way with the constructed diagrams of figs. 3–8, it is seen that the three curves are not represented in any of the diagrams of figs. 3, 4, 5, and 8. Fig. 7, however, shows a slight resemblance, while in fig. 6 there are curves which resemble more

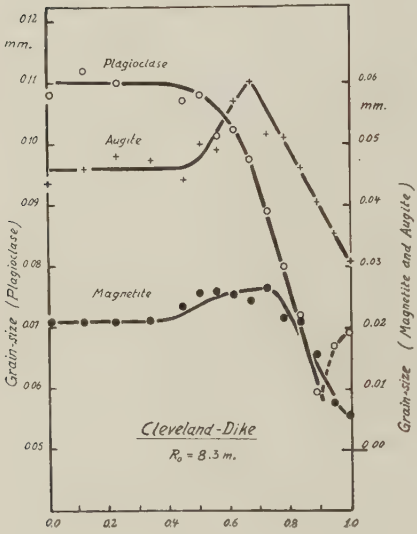

Fig. 9

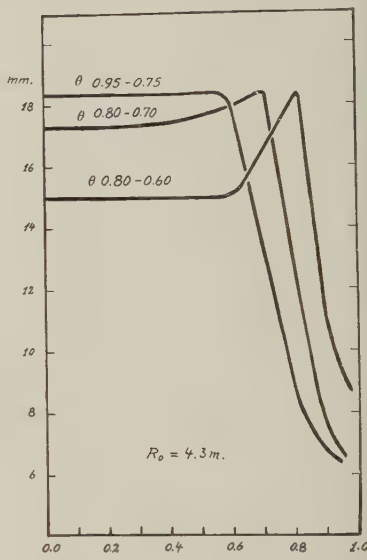

Fig. 10

Fig. 9. Crystal-size variation in the Cleveland dike (Great Ayton, Yorkshire) of plagioclase, augite, and magnetite.

Fig. 10. Constructed diagram showing crystal-size variation in a dike of $R_0 = 4{\cdot}3$ metres for various temperature ranges.

closely those which have been observed in the dike (fig. 9). The curve for plagioclase resembles the curve constructed for θ 0·9–0·8, magnetite that for θ 0·8–0·7, and augite that for θ 0·7–0·6. It must be expected, therefore, that the measured curves will very closely resemble curves constructed for a dike of half a thickness R_0, somewhere in between $R_0 - 5$ m. (fig. 7) and $R_0 - 4$ m. (fig. 6), but nearer to the latter thickness. Curves have been constructed for various thicknesses, and it is found that a dike of $R_0 - 4{\cdot}3$ m. shows curves of crystal-size variation which give the best coincidence with those observed in nature: the plagioclase curve is the same in type as the one constructed for the temperature range θ 0·9–0·8, the magnetite curve resembles closely the

curve for θ 0·8–0·7, and the augite curve that for θ 0·75–0·65. This would mean that the bulk of these minerals has crystallized approximately in the respective temperature ranges. In order to be more accurate, however, the textural relationship of the minerals has to be taken into account. It is obvious that most of the augite and magnetite has crystallized after the plagioclase, although sometimes a mutual intergrowth of magnetite and augite with plagioclase is observed. This illustrates that part of the plagioclase had not finished growth at a time when some of the magnetite, as well as the augite, had already developed. The temperature range in which plagioclase crystallized, therefore, should extend lower down, and the one for augite higher up.

Curves for R_0 – 4·3 m. have been constructed, representing variation of crystal-size when crystallization took place in correspondingly wider temperature ranges. (Cooling-velocities for such wider ranges are given in table I). Omitting all constructed curves which do not fit the curves of fig. 9, a diagram of those which fit is given in fig. 10. It is arranged side by side with fig. 9 to simplify comparison.

As nearly as possible the plagioclase curve corresponds in type to that constructed for a temperature range of θ 0·90–0·75, the one for magnetite to the curve for θ 0·80–0·70, and the augite curve to the curve constructed for θ 0·80–0·60. This means that in a tholeiitic magma *most* of the groundmass crystals have crystallized in the following temperature ranges. The temperatures in °C. corresponding to the θ-values are calculated on the assumption of an intrusion temperature $T_m = 1000°$ C. and an initial country-rock temperature T_c – 25° C.

plagioclase in θ 0·90–0·75 = 903–756° C.
magnetite in θ 0·80–0·70 = 805–708
augite in θ 0·80–0·60 = 805–610

These results are in conformity with the intersertal texture and its slight deviations. They are also in agreement with petrographical observations. It has often been noticed that in basaltic magmas the crystallization ranges of plagioclase and augite must have overlapped each other. Concerning magnetite, it has often been assumed that magnetite always crystallizes very early in magmas. This does not hold for gabbroic magmas, as H. L. Alling (1) and others have pointed out. A. Streng observed sixty years ago that, in certain German diabases, magnetite had crystallized after plagioclase and olivine. In the tholeiite, magnetite has definitely crystallized after the crystallization of plagioclase had commenced.

It has to be considered now if the results derived from interpretation of crystal-size variation are in agreement with our knowledge derived from physico-chemical data. On the basis of N. L. Bowen's (3) investigation of the ternary system albite–anorthite–diopside, T. F. W. Barth (2) has further developed a picture of crystallization of basaltic magma. According to him, a basaltic magma can be regarded, at a first approximation, as a point within the quaternary system albite–anorthite–diopside–hypersthene. It depends on the chemical composition of the magma if either plagioclase or pyroxene starts to crystallize first. During the process of crystallization the composition of the melt changes gradually, and when the cotectic surface is reached simultaneous crystallization of both minerals along the two-phase plane takes place. Barth (2) has fixed the position of the cotectic surface within the interior of the quaternary system and has expressed its position by the equation

$$\mathrm{Ab}' + 2\ \mathrm{Di}' + 2{\cdot}3\ \mathrm{Hy}' = 123.$$

In applying this equation, the norm of the rock has first to be calculated from the chemical analysis, then An, Ab, Di, and Hy are recalculated to 100, which gives Ab′, Di′, and Hy′. If the sum of these terms in the above equation is greater than 123 pyroxene has crystallized first, if less plagioclase.

This calculation has been carried out for the rock from Great Ayton (chemical analysis in (4) and (9)) and from two other localities of which A. Holmes (4) gives the norms. The sum of the above equation for rocks of different localities but all representing the tholeiite of the Cleveland dike is: Great Ayton, Yorkshire, 95·5; Bolam, Durham, 115·9; Boldon, Durham, 107·0. The sum is always less than 123 and therefore, according to Barth, plagioclase should start to crystallize before pyroxene. This also is the conclusion drawn from the interpretation of crystal-size variation.

While plagioclase crystallizes, the composition of the system is gradually altered towards the cotectic surface. When this is reached, both plagioclase and pyroxene crystallize together. The same conclusion has been arrived at from our method. But from this it follows that *most* of the plagioclase finished crystallization well before the bulk of the pyroxene. This can be understood, as plagioclase crystallization was initiated much earlier, and a good deal of the mineral had already separated before pyroxene started to grow. According to the quaternary system, plagioclase cannot completely cease to crystallize before pyroxene. It should be stressed here, again, that the temperature range

given for the crystallization of plagioclase, for example, does not refer quantitatively to all the plagioclase but, according to the method, to the majority of these crystals. Therefore, this method does not exclude the possibility that a smaller percentage of the plagioclase has crystallized at temperatures below θ 0·75 along with pyroxene, until the end of the crystallization. The percentage of plagioclase which might have crystallized below θ 0·75 until θ 0·60 can be approximately calculated from our curves.

The percentage of crystals growing at lower temperatures and having consequently a mean size different from that of the majority of crystals crystallized in the higher range of θ 0·90 0·75 cannot have been greater than the percentage which would markedly alter the character of the curve. The calculations show that up to 25% of the plagioclase crystals could have grown in the lower temperature range of θ 0·75–0·60; and a good deal, or perhaps all, of this percentage may have done so. On the other hand, at least 75%, or by far the greater part, has crystallized in the range of θ 0·90–0·75.

Corresponding calculations have been made for magnetite and augite. It was concluded that not more than 5% of augite could have crystallized in the higher range of θ 0·9–0·8, and probably none has done so. Concerning magnetite, up to 30% could have crystallized in the lower temperature range of θ 0·7–0·6, and some of it may have done so.

Thus the conception of crystallization in a tholeiitic magma, which has been mainly derived from the study of crystal-size variation in a dike, can be summarized in a diagram showing the temperature ranges in which the major and minor quantities of the groundmass minerals have crystallized. If the sharp steps in this diagram (fig. 11) are smoothed out into a curve, as done for plagioclase, the picture is likely to give a good idea of the crystallization process. It should be borne in mind, however, that about 40% of the magma has not crystallized at all during the cooling process, but has remained as a glass, which is no longer of basaltic composition.

In fig. 11 all of *each* groundmass crystal is represented as 100%. Let us now consider the crystallization process by taking all constituents of the rock as 100%. The tholeiite of Great Ayton shows the following composition in vol. %. These measurements agree with the data of Cleveland dike rocks from other localities which have been provided by Holmes (4), viz. phenocrysts 4, plagioclase 29, pyroxene 22, magnetite 4, mesostasis 41 vol. %. Using the results represented in fig. 11 the

following steps of crystallization with decreasing temperature are obtained:

TABLE II. Amounts of crystallized materials in the Cleveland dike at temperatures indicated by θ-values.

	θ 0·9.	θ 0·8.	θ 0·7.	θ 0·6.	$\theta < 0{\cdot}6$.
Phenocrysts	4	4	4	4	4 vol. %
Plagioclase	—	15	26	29	29
Pyroxene	—	—	11	22	22
Magnetite	—	—	3	4	4
Mesostasis...	—	—	—	—	41
Remaining melt in vol. %	96	81	55·5	40·5	0

In this table the figures represent volume %. It is also clearly seen how in the remaining melt the importance of the 41% of highly siliceous material which later forms the mesostasis becomes greater with progressing crystallization.

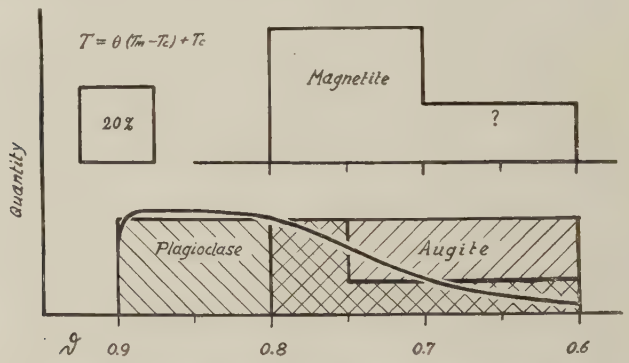

FIG. 11. Diagram showing crystallization of the groundmass minerals in the tholeiitic magma. (Quantity of crystals and temperatures, θ-values, are represented. All of each individual mineral is given as 100%.)

The general outline of crystallization is, as has been discussed, in full agreement with physico-chemical deductions. It should be noted, however, that in the first stage of crystallization of a basaltic magma, the quaternary system gives quite a reliable idea of the process, but with progressing crystallization the composition of the melt changes markedly, so that the late differentiates of tholeiitic magma are sub-alkalic, almost granitic in character as has been shown by W. Q. Kennedy (5) and F. Walker (10). This means that during crystallization the composition of the remaining melt changes gradually from the basalt- to the granite-system, which is a rather complicated process to deal with synthetically.

But synthetic work in connexion with the results derived from the interpretation of crystal-size variation will be undertaken.

Comparison of the tholeiitic magma with other magmas should be of great interest. This will be done first of all with the olivine-basalt magma, thus making possible a comparison between the two primary parent basaltic magmas postulated by W. Q. Kennedy (5). The ranges of crystallization of the bulk of the main constituents will probably be different. This presumption is supported by the interpretation of size variations across an olivine-diabase dike measured by H. L. Alling (1). A preliminary and approximate evaluation of temperature ranges in which most of the olivine, plagioclase, and augite crystallized has been communicated by the writer (12). But more accurate results are expected from the study of olivine-dolerite dikes from Scotland which is in progress.

Viscosity of magmas.

The curves of figs. 3–8, representing crystal-size variation with distance from the margin, refer to a certain equal viscosity for all the various dike thicknesses for which curves have been constructed. These dikes may be called 'comparison dikes'. If the viscosity of a magma was different from that of the comparison dike, then the size variation will not be the same in the natural as in the comparison dike if both are of the same thickness. A dike of $R_0 = 8$ m., for instance, having a greater viscosity than the comparison magma, shows crystal-size curves which are not similar to those constructed for a dike of the same $R_0 = 8$ m., but for a dike of $R_0 < 8$ m. This has been observed with the Cleveland dike. It is of $R_0 = 8{\cdot}3$ m. and the crystal-size curves have been found to be similar to those of a comparison dike of $R_0 = 4{\cdot}3$ m. (figs. 9 and 10). This means that the tholeiite magma has had a higher viscosity than the comparison magma. On the other hand, for an olivine-diabase dike at Ausable Forks, Essex Co., New York, (1) of $R_0 = 1{\cdot}7$ m., the crystal-size curves were found to resemble those of a comparison dike of $R_0 = 4$ m. (12). This means that the viscosity of this olivine-diabase magma has been smaller than that of the comparison magma, and thus has been definitely smaller than that of the tholeiite magma. This deduction is in full accord with our current conception on viscosities of magmas.

Imagining an olivine-dolerite magma of low viscosity and a tholeiite magma of higher viscosity each forming dikes of the same thickness, let us say $R_0 = 2$ m., the olivine-dolerite will show pronounced varia-

tions of crystal-size with distance from the margin (corresponding about fig. 7; $R_0 = 5$ m.), while the tholeiite dike will show hardly any (corresponding about fig. 3; $R_0 = 1$ m.). This has often been observed in the field and is due to the differences in viscosity of these two magmas.

A little more on viscosity of magmas has been said in (12), and it is proposed to deal with it more fully when further investigations on basaltic and other dikes are completed.

Acknowledgements.—My gratitude is expressed to Professor W. Q. Kennedy for permitting me to work in his Department in the University of Leeds and to him and Professor C. E. Tilley for stimulating discussions.

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Notes on the mineralogy and geochemistry of zinc.

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THE ionic radius of zinc (0·83 Å.) is identical with that of divalent iron (0·83 Å.) and nearly the same as that of magnesium (0·78 Å.). One would therefore expect zinc to be mineralogically closely related to iron and magnesium. It is, however, well known that this is not the case. An examination of a list of the zinc minerals which have so far been described shows that only in a few cases are the corresponding isomorphous ferromagnesian species known. As a rule zinc minerals and iron-magnesium minerals with corresponding chemical formulae are entirely different in their crystal-structure.

One might also anticipate that the zinc present in the earth's crust would be completely camouflaged in the ferromagnesian minerals, in the same way as gallium (0·62 Å.), which is about a third as common as zinc, is camouflaged in the minerals of aluminium (0·57 Å.).[1] In the case of aluminium and gallium the camouflage is a complete one, and gallium does not form minerals of its own at all. Zinc, however, is only to a small degree camouflaged in the ferromagnesian minerals in spite of the similarity of ionic radii between zinc on the one hand and iron and magnesium on the other. This is well illustrated by a recent investigation of an intergrowth of blende and Mn-Fe-garnet from a granite-pegmatite dike on the island of Kimito, Finland.[2] The two minerals have obviously been in equilibrium during their formation, and the garnet must be supposed to be 'saturated' in zinc. The content of ZnO in the garnet is nevertheless found to be smaller than 0·01%, giving a distribution coefficient of zinc between Mn-Fe-garnet and blende which is very low indeed.

The more easily a rare element is camouflaged in the minerals of common elements the less accessible it will be for industrial purposes. An indication of the tendency of any element to be camouflaged is

[1] V. M. Goldschmidt and C. Peters, Nachr. Gesell. Wiss. Göttingen, Math. phys. Kl., 1931, p. 165.

[2] O. Knorring, Compt. Rend. Soc. Géol. Finlande, 1946, vol. 19, p. 77. [M.A. **10**-420.]

therefore given by the extent to which that element must be concentrated compared with its average frequency in the lithosphere to give a deposit worth mining, and the greater the concentration factor, the smaller is the tendency to camouflage. The elements Nb, Cu, and U, which are usually regarded as being camouflaged only to a very small extent, have factors not greater than 200–300, while Sn has to be concentrated 1000 times to give a workable deposit. For Zn the factor is as high as 3000, about the same as for Au (2000) and Ag (5000).

This high figure, together with the fact that zinc deposits on the borderline of workability are very numerous and scattered all over the world, clearly demonstrate that zinc is not easily trapped in ferromagnesian minerals by incorporation in their crystal lattice.[1]

To the writer's knowledge no explanation has so far been given for this unexpected behaviour of zinc. A study of the crystal chemistry of the zinc minerals, as far as this is known, seems, however, to offer a simple solution to the problem.

Blende and wurtzite, ZnS.—In these minerals Zn occurs in four-coordination, each zinc atom is surrounded tetrahedrally by four sulphur atoms, and vice versa. The distance between Zn and S is in both cases 2·35 Å., and the two minerals are structurally related in the same way as a cubic close-packing is related to a hexagonal close-packing. The corresponding Fe^{II} mineral, pyrrhotine (or troilite), has a lattice of NiAs-type with Fe^{II} in six-coordination.

Zincite, ZnO, has a structure closely related to that of wurtzite. Each Zn atom is surrounded by four tetrahedrally arranged O atoms. The distance between Zn and O is 1·96 Å. These facts are not in agreement with an ionic type of binding, for if ZnO were an ionic compound one would expect the distance between Zn and O to equal the sum of the ionic radii of these elements, 0·83 Å + 1·32 Å. = 2·15 Å. Moreover, because of the relative sizes of the two ions one would expect six-coordination instead of four-coordination as is the case with periclase

[1] According to V. M. Goldschmidt (Vid.-Akad. Skr. Oslo, I. Kl., 1938 for 1937, p. 81) the average content of zinc in the earth's crust is 40 g./ton, mainly bound in ferromagnesian minerals in igneous rocks, augites, amphiboles, and especially biotite. The vast bulk of igneous ferromagnesian minerals should make their content of zinc the one important factor for the calculation of the above figure. It is quite possible, however, that zinc, contrary to Goldschmidt's view, is present in igneous rocks as submicroscopic crystals of blende deposited on the surface of the rock-forming minerals (H. Neumann, Econ. Geol., 1948, vol. 43, p. 83) instead of being present in solid solution in augites, amphiboles, and biotite. Blende is reported as a rare mineral in igneous rocks, and is certainly not uncommon in granite-pegmatite dikes.

and artificial FeO. The quotient between the ionic radii of Zn^{2+} and O^{2-} is 0·629, and six-coordination can be shown by geometrical consideration to be the stable coordination when the quotient between the radii of the cation and the anion is between 0·414 and 0·732. The slightly too short inter-atomic distance might easily be explained by a shortening of the radius of one or both of the elements zinc and oxygen,[1] but this cannot account for the abnormal coordination number.

Even if one makes the highly improbable assumption that only the radius of Zn is shortened while that of O remains constant, which would favour four-coordination more than any other assumption, the quotient between the radii would be 0·485 and thus well within the limits of six-coordination. For geometrical reasons undirected chemical bonds in zincite are therefore impossible, and one is forced to assume that *zinc is bound to oxygen by covalent bonds directed in space towards the corner of a tetrahedron.* In accordance with such an interpretation Pauling and Huggins[2] have used the distance between Zn and O in zincite for the calculation of the covalent 'tetrahedral radius' of oxygen, while the inter-atomic distance in blende has been used for the calculation of the 'tetrahedral radius' of zinc.

In *Gahnite*, $ZnAl_2O_4$, zinc is again found within a group of four tetrahedrally arranged oxygen atoms. Gahnite belongs to the 'normal' type of spinels with Zn in four-coordination and Al in six-coordination.[3]

Whether *Franklinite*, $ZnFe^{III}{}_2O_4$, is a 'normal' spinel or a spinel with 'variate atom equipoints' cannot be determined by X-ray methods because of the great similarity in scattering power of Zn and Fe. It is hardly unjustified to assume that Zn occurs in four-coordination as this is the case with the great majority of zinc minerals with known coordination number.

Hetaerolite, $ZnMn_2O_4$, has a distorted spinel structure. For the same reason as for franklinite the coordination number is unknown, but may be four.

Smithsonite, $ZnCO_3$, is isomorphous with the corresponding iron and magnesium minerals, chalybite, and magnesite. Zinc is surrounded by

[1] The radii used above for the calculation of the hypothetical distance between Zn and O, if ZnO were an ionic compound, are the ionic radii for Zn and O in six-coordination. For four-coordination the hypothetical distance should be reduced by about 6%, if, indeed, elements in four-coordination are ever bound by purely ionic bonds.

[2] L. Pauling and M. L. Huggins, Zeits. Krist., 1934, vol. 87, p. 205.

[3] T. F. W. Barth and E. Posnjak, Journ. Washington Acad. Sci., 1931, vol. 21, p. 255; Zeits. Krist., 1932, vol. 82, p. 325. [M.A. 5–179.]

six oxygens forming a somewhat distorted octahedron. Smithsonite is the only mineral containing zinc which is with certainty six-coordinated, apart from some exceedingly rare silicates (see later).

In *Willemite*, Zn_2SiO_4, zinc is surrounded by four tetrahedrally arranged oxygen neighbours, while the corresponding iron and magnesium minerals, fayalite and forsterite, are six-coordinated. The distance between zinc and oxygen is 1·92 Å., and similar considerations as for zincite lead to the conclusion that the chemical bonds of zinc must be covalent and directed towards the corners of a tetrahedron.

Hemimorphite, $Zn_4Si_2O_7(OH)_2.H_2O$, contains zinc tetrahedrally surrounded by four oxygens, three of which belong to Si_2O_7 groups, and one to a OH group. No ferromagnesian mineral with a corresponding formula is known.

Hardystonite, $Ca_2ZnSi_2O_7$, is isomorphous with the corresponding magnesium mineral, åkermanite, $Ca_2MgSi_2O_7$, and is an exception to the rule that zinc minerals are not isomorphous with corresponding ferromagnesian minerals. In this case, however, it is the coordination number of the magnesium, not the zinc, which is exceptional, as these elements are found in åkermanite and hardystonite surrounded tetrahedrally by four oxygens, which is normal as far as zinc is regarded, but highly exceptional for magnesium, whose normal coordination number is six.

Larsenite, $PbZnSiO_4$, a rare Franklin Furnace mineral, is a member of the olivine group, and contains zinc surrounded by six octahedrally arranged oxygen neighbours.

The structures of *Hodgkinsonite*, $MnZn_2SiO_4(OH)_2$, and *Leucophoenicite*, $(Mn,Mg,Zn)_8Si_3O_{12}(OH)_4$, are unknown. Both are rare and found at Franklin Furnace only. They are possibly isomorphous with the corresponding magnesium minerals, norbergite and humite, and, if so, would contain zinc in six-coordination.

The above data show that zinc is bound in four-coordination in the great majority of its minerals, and that this is the case with all the more common zinc minerals apart from smithsonite. Zinc analogues to the great number of ferromagnesian minerals are non-existent, and the reason for this is obviously that zinc has a very pronounced tendency to form covalent tetrahedrally directed bonds, while divalent iron and magnesium tend to form minerals with ionic bonds where the coordination number is six because of the size of the ions.

As a consequence of this one would expect zinc to be taken into solid solution preferably by minerals in which it can replace elements in

four-coordination. A survey of the mineral analyses where zinc is determined demonstrates that this is really the case. The writer has omitted analyses showing only a few tenths per cent. of zinc because impurities in the analysed material and analytical errors may easily account for these small figures. When a small amount of zinc is reported in only one of a long series of analyses of a certain mineral species, this mineral is also omitted from the list given below.

The following minerals are found to contain an appreciable amount of zinc: stromeyerite, CuAgS; metacinnabar, HgS; polybasite, $Ag_{16}Sb_2S_{11}$; pearceite, $Ag_{16}As_2S_{11}$; tetrahedrite, $(Cu,Fe,Ag,Zn)_{12}(Sb,As)_4S_{13}$; germanite, (Cu,Ge,Fe)(S,As); jamesonite, $Pb_4FeSb_6S_{14}$; zinckenite, $Pb_6Sb_{14}S_{27}$; danalite, $(Mn,Fe,Zn)_8Be_6Si_6O_{24}S_2$; chromite, $FeCr_2O_4$; zinc-spinel, $(Mg,Zn,Fe)Al_2O_4$; hausmannite, $MnMn_2O_4$; and nigerite, $(Zn,Mg,Fe^{II})(Sn,Zn)_2(Al,Fe^{III})_{12}O_{22}(OH)_2$.

The structures of polybasite, pearceite, jamesonite, and zinckenite are not known in detail and nothing can be said about the coordination number.

Stromeyerite is isomorphous with the low-temperature modification of chalcosine. The structures of the two modifications of chalcosine are not too well known. A study of the system Cu_2S–CuS has shown, however, that reversible transitions exist between chalcosine and digenite.[1] Digenite has an antifluorite structure with copper in four-coordination, and the ease with which the transition chalcosine $\rightleftharpoons$ digenite takes place with change in temperature or chemical composition indicates a four-coordinated structure for chalcosine as well, and hence for stromeyerite.

The regular Zn-content of metacinnabar illustrates our point very clearly. This mineral has a lattice of the blende type with Hg in four-coordination. Cinnabar, on the other hand, has a distorted sodium chloride structure where Hg is found within an octahedral group of six sulphur atoms. In the four-coordinated metacinnabar Zn is taken into solid solution in quantities up to nearly 5%, while Zn has never been reported from the six-coordinated cinnabar at all.

Zinc is found in most tetrahedrites, occasionally in quantities up to 10% by weight. It replaces four-coordinated copper. Germanite has a lattice of the blende type where zinc replaces copper and germanium in four-coordination. The lattice of danalite is similar to that of sodalite and will, therefore, contain zinc in four-coordination.

It is not known if chromite is a spinel of 'normal' type or if it is

[1] N. W. Buerger, Econ. Geol., 1941, vol. 36, p. 19. [M.A. 8–254.]

a spinel with 'variate atom equipoints'. Zinc will probably enter the four-coordinated positions of the lattice. Hausmannite has a distorted spinel structure and is isostructural with hetaerolite. Zinc probably replaces four-coordinated manganese. The positions of the atoms in nigerite (Min. Mag. **28**–118, 129) are not determined, but an arrangement of O and OH is proposed giving tetrahedral and octahedral interstices. A possibility for zinc to replace a four-coordinated element is therefore indicated.

With the above list of minerals commonly containing zinc the tendency of this element to selective replacement of atoms in four-coordination is well established.

As an exception may be mentioned that at Franklin Furnace and Sterling Hill zinc is also found in a series of minerals replacing elements in six-coordination, such as brucite, pyrochroite, manganosite, zinc-amphibole, zinc-olivine (roepperite), and zinc-pyroxene (jeffersonite). An attempt to explain this phenomenon would imply a discussion of the genesis of these extraordinary deposits, and would be out of place in this paper. Excluding deposits of smithsonite, which is always of secondary origin, these two deposits are exceptional as containing six-coordinated zinc in appreciable amount, and even here nearly all the zinc present is four-coordinated in the ore-forming minerals franklinite, willemite, and zincite.

There is possibly another exception to the rule as well, which may be of far greater importance. C. S. Ross[1] has recently described zinc-bearing montmorillonite (sauconite) from Pennsylvania, and deduces from his analyses that zinc enters the octahedral positions of the lattice and not the tetrahedral ones. That clay minerals can contain zinc in solid solution may be important for the understanding of the geochemistry of Zn in the sedimentary cycle but, so far, too few data are known about the amounts of zinc in slates and clays to take this problem up for discussion.

Our present knowledge about the crystal chemistry of zinc minerals and minerals containing zinc in solid solution is limited. Many of the species mentioned above are not known in detail, and some zinc minerals have not been mentioned at all because they have never been examined by X-ray methods. In spite of this lack of information, however, the evidence summarized here seems to the writer to justify the conclusion that the one important factor which characterizes and stamps the mineralogical and geochemical behaviour of zinc is that the element

[1] C. S. Ross, Amer. Min., 1946, vol. 31, p. 411. [M.A. **10**–26.]

tends to form covalent bonds directed in space towards the corners of a tetrahedron.

Most of the more common elements in the lithosphere tend to form ionic bonds with oxygen, and it is a well-established principle that the size of their ions decides their geochemical behaviour. This principle is not valid in a case like that of zinc where the element tends to form covalent bonds. The primary principle of geochemical classification of the elements must obviously be their tendency to form ionic, covalent, or metallic bonds. Secondarily, elements forming ionic compounds may be classified according to ionic radii, and elements forming covalent bonds according to spatial properties of their bonds.

Apart from an important investigation by F. E. Wickman[1] on the geochemistry of the elements in sedimentary rocks, the geochemical importance of the character of chemical bonds has been hardly discussed. No doubt the reason for this is that our understanding of the nature of chemical bonds is somewhat unsatisfactory, and that we at present have no means to measure quantitatively the tendency of any element to form a certain type of chemical bond. A method of measuring such a tendency would have a wide application in geochemistry, and one of the first results would probably be the establishment of a sound theoretical basis for the classification of chemical elements as siderophile, chalcophile, lithophile, and atmophile,[2] which classification is at present purely empirical.

[1] F. E. Wickman, Arkiv Kemi, Min. Geol., 1945, vol. 19 B, no. 2. (Preprints dated 1944.)

[2] V. M. Goldschmidt, Vid.-Akad. Skr. Oslo, I. Kl., 1923, no. 3. [M.A. 2-159.]

Dickite from the Witwatersrand gold mines.

By J. J. Frankel, D.Sc., F.G.S.
University of Natal, Durban, South Africa.

[Read January 26, 1949.]

THE occurrence of dickite in the gold-bearing rocks of the Witwatersrand system was first reported by Mr. H. C. M. Whiteside.[1] In addition, among the many mineral samples given to me by students of the Witwatersrand Technical College, Johannesburg, were several dickite specimens from mines all along the Witwatersrand area. Dickite may therefore be regarded as fairly widespread in the rocks of at least the Main-Bird series, although not in large quantity.

The only occurrence of which a detailed record is available is that from the Daggafontein mine. Little is known of the other samples except from the immediate mineral associations. It is, however, clear that all the occurrences are of hydrothermal origin.

Although the various specimens do not differ greatly in any particular property, it is considered best to describe the associations and macroscopic features of each specimen separately.

Daggafontein mine. The dickite, which is in rounded lumps, was embedded in a greenish-grey clay; this material was composed of quartz crystals and a chloritic mineral none of which is available for detailed study. The dickite lumps are irregularly streaked with grey chlorite in which are embedded small pyrrhotine crystals and small kidney-shaped and rounded particles of a lustrous black organic material. No positive identification was given for this substance by Whiteside, who suggested it resembled grahamite on the grounds of specific gravity. Careful determinations on a sample in my possession gave a specific gravity of 1·27. This is probably slightly high owing to a small amount of complex impurity which is left as an ash after ignition. In the absence of any detailed analysis its true nature remains for the present unknown. The other minerals present have been described by Whiteside previously, but mention must be made of a few small cubes of silvery gersdorffite, which is possibly the mineral originally described as galena.

[1] H. C. M. Whiteside, 1941. An unusual suite of minerals from a vug in a quartz vein in the Kimberley series, Daggafontein mines, Ltd. Trans. Geol. Soc. South Africa, 1942, vol. 44 (for 1941), pp. 121–126. [M.A. 9–65.]

Rand Leases.—Two specimens from different parts of this mine show the same mineral associations. The dickite as received was adhering to aggregates of small quartz crystals growing from the walls of quartz vugs. None of the quartz crystals was quite like those from Daggafontein; most of them were terminated at one end only. There were, however, several crystals absolutely water-white and doubly terminated. An interesting feature is the inclusion of irregular vein-like growths of a lustrious black organic material in some of these crystals.

With the dickite are minute crystals of pyrite as cubes, pyrrhotine as books of hexagonal plates, and chalcopyrite as slender and flat crystals. Much sooty-like 'carbon' is scattered among the dickite aggregates.

Langlaagte Estates.—This sample consisted of two small pieces of quartz vug wall with dickite and sulphide crystals similar to those from Rand Leases.

Consolidated Main Reef mine.—The specimen of dickite from this mine has a more interesting appearance than those from the other mines. Dickite is present as a thick layer of drab green colour moulded on the conglomerate reef itself as well as on to imperfectly formed quartz crystals and nodular pyrite.

Crystallographic and optical properties.

Little can be added from the detailed study of all the Witwatersrand specimens to the data already on record for dickite. In the classic work so carefully carried out by Dick[1] and the subsequent investigation by Ross and Kerr[2] the mineral has been described most thoroughly.

Under the microscope the various samples show practically perfect crystals of a fascinating beauty. Forms and habits identical with those drawn by Dick of the Anglesey material are seen. The dominant crystal faces are the basal pinakoid (001) and the prism (110). The clinopinakoid (010) is present on the larger crystals (fig. 1 *c*), but it is poorly developed and almost entirely absent on the smaller crystals. This is particularly so of those from the Daggafontein mine (fig. 1 *b*). The orthopinakoid (100) is poorly developed on relatively few crystals. The pyramids (111) and (*hkl*) are recognizable, the former considerably more frequently. The presence of the dome (0*kl*) is doubtful.

[1] A. B. Dick, On kaolinite. Min. Mag., 1888, vol. 8, pp. 15–27. Supplementary notes on the mineral kaolinite. Ibid., 1908, vol. 15, pp. 124–127.

[2] C. S. Ross and P. F. Kerr. The kaolin minerals. Prof. Paper U.S. Geol. Surv., 1931, no. 165-E, pp. 151–176. [M.A. 5–359.]

Some of the optical properties determined in sodium-light are tabulated below. In addition, the trace of c (001) on b (010) was measured as 22 to 23°. For comparative purposes the properties of a specimen of dickite separated from a clay from the Middelburg district, Transvaal, are added.[1]

	α.	β.	γ.	Extinction on b (010).	$2V\gamma$
1	1·561	1·564	1·567	14°	69°
2	1·560	1·564	1·567	16°	69°
3	1·561	1·563	1·568	15°	67°
4	1·560	1·563	1·567	16 to 17°	66 to 68°

1. Dickite, Daggafontein mine; 2, Rand Leases;
3. Rand Leases; 4. Middelburg district, Transvaal.

(Refractive indices all ±0·001.)

Chemical Composition.

A chemical analysis was made previously of a 'green dickite' from the Consolidated Main Reef mine and more recently the specimen from the Daggafontein mine was analysed.

	1.	2.	3.	(Atoms on basis 9(O,OH))	
SiO_2	41·90	45·49	45·58	1·97	
TiO_2	trace	none	—		
Al_2O_3	33·12	40·91	40·99	2·07	
Fe_2O_3	0·93	—	—		
FeO	10·28	0·17	—		Si,Al 2·00
MnO	0·23	n.f.	—		Al 2·04
MgO	0·03	trace	—		(OH) 3·97
CaO	0·12	none	—		
H_2O^+	13·24	13·92	13·94	3·97	
H_2O^-	none	0·01	—		
Cr_2O_3	n.f.	trace	—		
	99·85	100·50	100·51		

1. Green dickite, Consoliated Main Reef mine. (Frankel, 1944.)
2. White dickite, Daggafontein mine.
3. Analysis 2, recalculated after removal of moisture and iron.

Dr. B. Wasserstein of the Union Geological Survey very kindly made a qualitative spectrographic analysis of the Daggafontein dickite and reported as follows. (The digits are rough arbitrary determinations of visual intensity of certain sensitive lines.) Pb 2, Fe 7, Cr 9, V 5, Ni 1, Mg 1, Ga 1. Absent—Mn, K, Li, Na, Rb, Ca, Ti, Sr, Ba, Sn, Co. Mo, Yt, &c.

Under the microscope the 'green dickite' is seen to be composed of perfect crystals of colourless dickite (fig. 1 *a*) surrounded by a green

[1] Determinations made on a sample kindly supplied by Dr. V. L. Bosazza some years back.

mineral of low birefringence with a mean refractive index of roughly 1·625. This green mineral makes up approximately 15 per cent. of the sample. A computation of its composition obtained by subtracting the theoretical composition of dickite from the analysis suggests a chloritic mineral rather than a variety of nontronite, which was a tentative suggestion made earlier.[1]

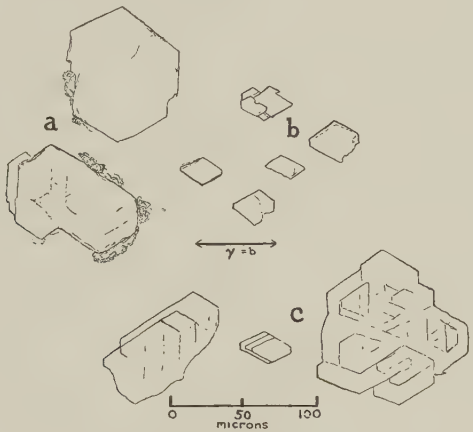

Fig. 1. Camera lucida drawings of dickite crystals.

a. Shows an association of colourless dickite partly surrounded by an irregular growth of a green chloritic mineral. Consolidated Main Reef mine.

b. Characteristic habit of the smaller crystals from the Daggafontein mine.

c. Crystals from Langlaagte Estates.

The ferrous oxide reported in the Daggafontein analysis is due to the presence of a minute amount of extremely fine pyrrhotine. The ferrous oxide was removed from the analysis and the recalculated values gave the formula of this dickite as $(Si,Al)_{2\cdot00}(Al)_{2\cdot04}(OH)_{3\cdot97}(O)_{5\cdot03}$ which may be compared with the theoretical figures of $Si_2Al_2(OH)_4O_5$.

Physical Properties.

Pressure on crystals between glass slide and cover-slip has revealed no direction of cleavage other than that of the perfect basal cleavage. The specific gravity of the Daggafontein material was found by suspension in a heavy liquid to be 2·61 to 2·62. In the hand-specimens the colour varies from dead white (Daggafontein) to a pale silvery-

[1] J. J. Frankel, On silicates and dusts from the Witwatersrand gold mines. Journ. Chem. Metall. Mining Soc. South Africa, 1944, vol. 44, pp. 169–177. [M.A. 9–103.]

grey (Rand Leases). The green colour of the Consolidated Main Reef specimen is of course due to the admixture of the unidentified green mineral. Under the microscope all the crystals are colourless and perfectly transparent.

The following table gives the crystal-sizes in microns (average of the maximum and minimum directions across the basal pinakoid).

	Large.	Small.	Average.
1	40	6	15μ
2	80	10	60
3	80	30	60
4	100	20	40
5	150	60	80
6	100	30	60

1, Daggafontein mine; 2, Rand Leases mine; 3, Rand Leases mine; 4, Langlaagte Estates; 5, Consoliated Main Reef mine; 6, Middelburg district, Transvaal.

Most of the samples are made up of individual crystals in parallel orientation with the basal pinakoid as contact face; and, as noted by Ross and Kerr, rotation of one crystal with reference to the other when basal pinakoid is the contact face is often observed. Single crystals are fairly abundant.

Staining tests with organic dyes gave the characteristic poor adsorption and no development of artificial pleochroism. Occasional shreds of kaolinite present in the specimens stand out sharply by contrast because of their reaction to the dyes.

X-ray powder photographs taken of several of the specimens show all the dickite lines clearly, including those of high order.

In all the examples from the Witwatersrand the mineral associations show that the dickite is of hydrothermal origin. It is anticipated that many more occurrences of dickite will be discovered in the course of mining.

The constitution of some Egyptian clays.

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[Communicated by Dr. G. W. Brindley; read January 27, 1949.]

Introduction.

THE Egyptian clays under consideration are obtained from two different localities. The Aswan clays are mainly concentrated in the neighbourhood of Aswan town in Upper Egypt and the Sinai kaolins from the Sinai Peninsula. The Aswan clays, namely: red Aswan clay, white Aswan clay, and siliceous Aswan clay, are transported clays, while Aswan kaolin is a residual clay. The Sinai kaolins are of obscure origin but most probably are transported clays. As is shown later, these are alunite-bearing clays not previously recorded in Egypt.

Petrographic examination.

Megascopic investigation of hand-specimens of the raw clays followed by petrographic examination of thin sections and of elutriated fractions, showed that quartz is the main constituent beside the clay minerals. It is abundant and of very small particle-size, and is evenly distributed in all the elutriated fractions. Iron compounds as well as some mica also occur. The red colour in some of these clays, especially in the red Aswan clay, is mainly due to iron compounds. Sinai kaolin, an alunite-bearing clay, shows coarser quartz grains and small gypsum veinlets.

The determination of free quartz.

Since all these clays contained quartz in appreciable amounts, a quantitative determination was necessary. This was first carried out using the method of estimation devised by Trostel and Wynne, 1940 [1]. The results obtained from three Egyptian clays using this method are as follows:

White Aswan clay.	Red Aswan clay.	Sinai kaolin.
20·8%	16·6%	7·8%

There are certain limitations regarding the accuracy of the method,

since microscopic investigations showed that the finer quartz fractions passed through the paper during filtration and thus a rather low value may be obtained. A centrifugal separation ought therefore to be made. A further defect, which may give rise to misleading results, arises from the dissolving effect of sodium hydroxide on any silica present in a chalcedonic form.

A more reliable quantitative determination of the free quartz was achieved by making use of the small thermal effect of the $\alpha \rightarrow \beta$ transition at 573° C. The amount of quartz was determined by measuring the heat evolved in this reversible transformation using a sensitive galvanometer. This method has been perfected by Grimshaw, Westerman, and Roberts, 1948 [2], and one of us (G. M. G.) was privileged to use their apparatus for the purpose of this investigation. The following results were obtained for the percentages by weight of free quartz in the Egyptian clays:

Siliceous Aswan clay.	Aswan kaolin.	White Aswan clay.	Red Aswan clay.	Sinai kaolin.
56 %	47 %	20 %	18 %	8 %

These results may be compared with the corresponding results obtained by the Trostel and Wynne method.

Identification of the clay minerals

The clay minerals present in these clays are of extremely small particle-size and could not be identified microscopically. For their industrial application, the determination of the kind of clay mineral present is important. The clay mineral component, as illustrated by Grim, 1939 [3], is the chief factor determining the physical properties of the clay; even a minor clay mineral constituent may play an important part in the characteristics of the raw clay material.

For such identification, several methods were used, some helping to place the clay in its group (e.g. the kaolin group of minerals) and others to identify the particular clay mineral.

Chemical analysis.

This is of rather limited value since the different clay minerals of a group have similar compositions. Nevertheless it seems to indicate broadly the type of clay mineral present. Chemical analysis has been limited to the determination of SiO_2, Al_2O_3, and water. Subtracting the

percentages of free quartz from the total silica we obtain the following results:

	Total SiO_2 %.	Free quartz %.	Combined SiO_2 %.	Al_2O_3 %.	H_2O %.
White Aswan clay...	50·54	20	30·54	32·0	10·05
Red Aswan clay ...	53·53	18	35·53	27·0	11·05
Sinai kaolin ...	29·10	8	21·10	36·0	14·00

When these percentages of combined SiO_2, Al_2O_3, and H_2O are reduced to their molecular proportions, the ratios of Al_2O_3:SiO_2:H_2O are as follows:

	Al_2O_3		SiO_2		H_2O
White Aswan clay	1	:	1·6	:	1·8
Red Aswan clay	1	:	2·2	:	2·1
Sinai kaolin	1	:	1	:	2·2

Generally the figures obtained are not inconsistent with the kaolin group of minerals. It is seen, however, that SiO_2 in the Sinai kaolin is very low, while the Al_2O_3 and H_2O contents are high. This is simply due to the occurrence of alunite beside the clay mineral, as will be shown later.

Cationic exchange measurements.[1]

As shown by Hendricks, 1945 [4], the cationic exchange properties of clays are of considerable value in placing them in their groups. For the Egyptian clays the total exchangeable cations were found by electrodialysis and by the ammonium acetate leachate method of Bray and Willhite, 1929 [5]. The results are as follows, expressed in milligram equivalents per 100 grams of the clay material:

White Aswan clay.	Red Aswan clay.	Sinai kaolin.
4·7	7·1	2·6

The cation exchange capacity was then determined by the method of Schollenberger and Dreibelbis, 1930 [6]. Results in milligram equivalent per 100 grams of the clay material are given below:

White Aswan clay.	Red Aswan clay.	Sinai kaolin.
8·8	12·3	9·6

These results suggest that the main clay minerals are of the kaolin group, which is in accordance with the previous chemical analysis.

[1] 'Cationic exchange' was suggested as better than 'base exchange' at the International Geological Congress, London, 1948, by Dr. J. S. Hosking.

Identification of the kaolin clay minerals.

To identify the individual kaolin clay minerals present, three different methods were used, namely (1) the rates of dehydration on heating, (2) differential thermal analysis, (3) X-ray powder analysis.

(1) *The rates of dehydration on heating.*

The loss of combined water on heating clays has long been a subject of investigation. In carrying out the test, a sample of 1 to 2 grams is

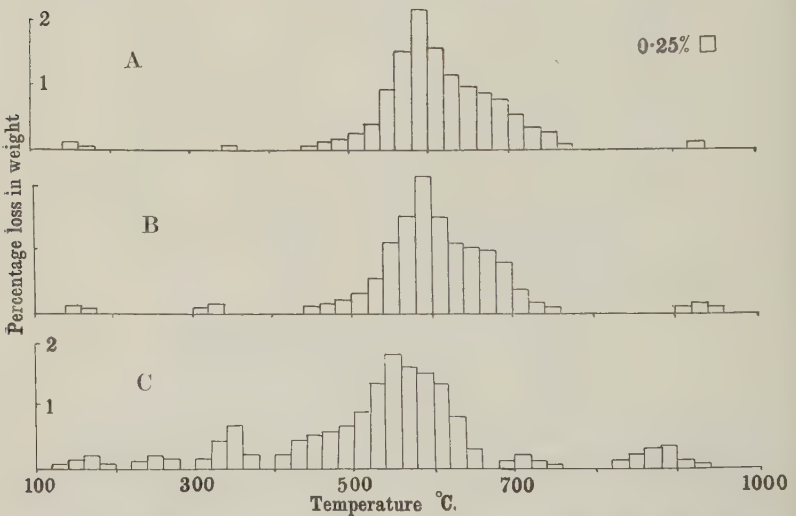

Fig. 1. Differential weight-loss diagrams. A, British standard kaolinite. B, European standard kaolinite. C, Utah halloysite.

suspended in an electrically-heated tube furnace by means of a platinum wire attached to one arm of a sensitive balance. The temperature of the furnace was measured by a platinum/platinum 13 % rhodium thermocouple placed with its junction opposite the middle of the suspended sample. The rate of heating was regulated to 10° C. per minute. Dry air was passed through the furnace at a rate of 5 litres per hour. The weight loss was recorded every 20° C. or after periods of 2 minutes. This technique was first applied to clay minerals of higher purity and later to the Egyptian clays. The results obtained were plotted as differential weight-losses against temperature in a diagrammatic manner.

(*a*) *Standard kaolinite and halloysite.*—Both the British standard kaolinite (china-clay 'Supreme') (fig. 1 A) and the European standard kaolinite (Zettlitz kaolinite) (fig. 1 B), show the beginning of a continuous weight-loss at 440° C., with a maximum weight-loss at 580° C. to 600° C.

In the case of Utah halloysite (fig. 1 C) the beginning of this continuous loss starts at 400° C., i.e. 40° C. lower than for kaolinite, and

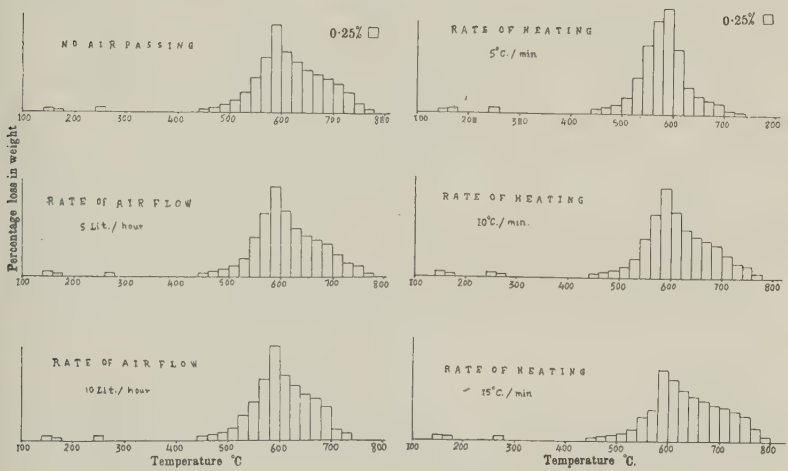

FIG. 2 FIG. 3

FIG. 2. Effect of variation of the rate of air-flow on the general shape of the differential weight-loss diagrams.

FIG. 3. Effect of variation of the rate of heating on the general shape of the differential weight-loss diagrams.

has its maximum at 540° C. to 560° C. In addition, as previously mentioned by Ross and Kerr, 1934 [7], it also shows a low-temperature water-loss up to 300° C. (The loss between 300° C. and 400° C. is due to a gibbsite impurity in the Utah halloysite sample.)

It is worth noting that neither the beginning of the continuous weight-loss, nor its maximum, is influenced by variation in the experimental conditions used, e.g. the variation of the rate of air-flow or the rate of heating. Figs. 2 and 3 show that such variations may only cause a change in the general shape of the diagram.

(*b*) *Aswan kaolin and siliceous Aswan clay.*—For these clays figs. 4 A and 4 B show the beginning of the continuous loss at 440° C. with its maximum at 580° C. to 600° C. in agreement with kaolinite. The

noticeable bulging on the right side of the Aswan kaolin diagram may be due to the presence of another clay mineral of the kaolin group, such as dickite.

(*c*) *White Aswan clay and red Aswan clay.*—In figs. 4 C and 4 D both clays show the beginning of a continuous loss in weight at 400° C. and

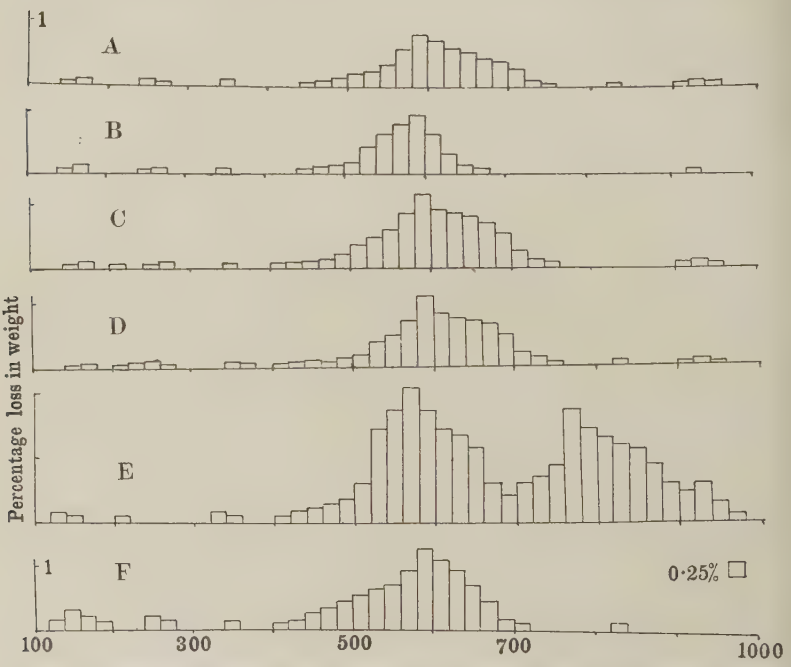

FIG. 4. Differential weight-loss diagrams. A, Aswan kaolin. B, Siliceous Aswan clay. C, White Aswan clay. D, Red Aswan clay. E, Sinai kaolin containing alunite. F, Sinai kaolin fireclay mineral.

a lower water-loss in the temperature range up to 300° C. and therefore resemble halloysite. On the other hand, the water seems to be more strongly held than in halloysite, since the maximum of the continuous weight-loss occurs at 580° C. to 600° C., resembling kaolinite. In other words, the left-hand side of the diagrams resemble halloysite and the right-hand sides resemble kaolinite. It thus seems that either there is a mixture of both minerals in these clays or we have here a case of a distinct mineral of an intermediate nature between kaolinite and halloysite, such as has been recently found by thermal analysis and by X-rays to occur in many British fireclays.

(*d*) *Sinai kaolins.*—Fig. 4 E shows the dehydration data for the Sinai kaolin which is later shown to contain alunite. Since both the clay mineral and the alunite lose water within the same temperature range it was found difficult to draw a definite conclusion about the kind of clay mineral present. It is, however, worth noting that this method of investigation in this case is very helpful in indicating the presence of alunite in clays from the loss of weight due to the evolution of sulphur trioxide between 700° C. and 1000° C. Identification of the clay mineral in Sinai kaolin was achieved by examining a second sample which did not contain alunite. This showed (fig. 4 F) the intermediate clay mineral previously found in white and red Aswan clays.

(2) *Differential thermal analysis.*

Thermal analysis using the differential technique has been widely used in distinguishing between individual members of clay groups, especially those of the kaolin group. Kaolinite and halloysite are characterized by a sharp and pronounced exothermic reaction at 980° C., while the kaolin mineral in many British fireclays shows a less sharp and rounded exothermic peak at 950° C. On the other hand, kaolinite, the fireclay mineral, and halloysite have endothermic peaks at 580° C., 555° C. to 565° C., and 550° C. respectively, as indicated by Grimshaw, Heaton, and Roberts, 1945 [8]. Thermal analysis of the Egyptian clays was carried out using their apparatus and applying their techniques. The following results were obtained:

(*a*) *Siliceous Aswan clay and Aswan kaolin* (figs. 5 A and 5 B).—The endothermic peak *b* in both cases suggests the presence of kaolinite. An extra deflection *d*, fig. 5 B, is observed with Aswan kaolin, which may be due to the presence of small amounts of dickite. The sharpness of the exothermic peak *c*, fig. 5 B, in the case of Aswan kaolin supports this kaolinite hypothesis, but the roundness of the exothermic peak *c*, fig. 5 A, of the siliceous Aswan clay may indicate a poor kaolinite or a mineral falling between kaolinite and the type of mineral found in fireclays.

(*b*) *White Aswan clay and red Aswan clay* (figs. 5 C and 5 D).—Both show a pronounced lower temperature peak, *a*, a V-shaped endothermic peak, *b*, and a rounded exothermic peak, *c* at 950° C. These results all suggest a fireclay mineral type. But the V-shaped endothermic peaks *b* occur in both at 575° C., which is a high temperature for the fireclay type of mineral shown by Grimshaw, Heaton, and Roberts, 1945 [8]. This may be taken either as an indication of the presence

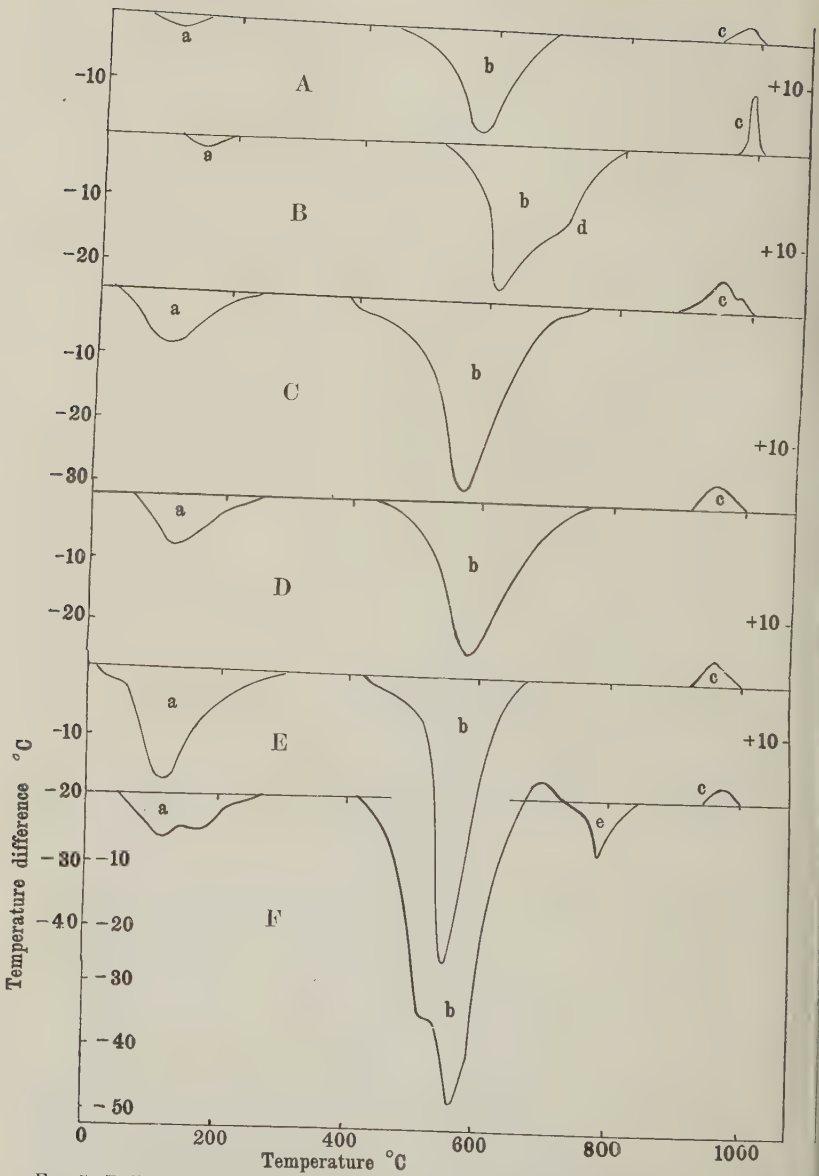

FIG. 5. Differential thermal analysis curves. A, Siliceous Aswan clay. B, Aswan kaolin. C, White Aswan clay. D, Red Aswan clay. E, Sinai kaolin fireclay mineral. F, Sinai kaolin containing alunite.

of some kaolinite or another fireclay mineral approaching the characteristic thermal behaviour of the kaolinite. This gives rise to a second exothermic peak at 980° C. in the white Aswan clay. This double-peak effect is, however, missing in red Aswan clay.

(*c*) *Sinai kaolins* (figs. 5 E and 5 F).—The curve of this Sinai kaolin, which is free from alunite, is shown in fig. 5 E. It is identical with the typical fireclay minerals detected by Grimshaw, Heaton, and Roberts, 1945 [8]. But when alunite is present, fig. 5 F, it is rather difficult to identify definitely the kind of clay mineral present. This is due to the influence of the water from the alunite which has its maximum peak at 570° C. However, the roundness of the exothermic peak, *c*, fig. 5 F, could be taken as an indication of a fireclay mineral. But this in some cases may give misleading results, due to the fact that when alunite is present with clays it has a reducing effect on their exothermic peaks. The endothermic peak, *e*, is also due to alunite.

(3) *X-Ray powder analysis.*

Since all the Egyptian clays under consideration contain appreciable amounts of quartz, purer clay mineral specimens were prepared from a suspension of the clay materials in distilled water after they had been allowed to settle for several hours.

The X-ray diffraction patterns were obtained using the 20 cm. semi-focusing camera, which was briefly described by Brindley and Robinson, 1946 [9] in connexion with their work on the structure of kaolinite. The results were as follows:

(*a*) *Aswan kaolin.*—Its pattern shows kaolinite and some mica. Dickite is not encountered and if present, as suggested by thermal analysis, the amount is less than about 5 %.

(*b*) *Siliceous Aswan clay.*—It is a very poor kaolinite. It could be even placed intermediate between kaolinite and the kaolin mineral which occurs in fireclays.

(*c*) *White Aswan clay and red Aswan clay.*—These were identified as typical fireclays. They are identical with the fireclay mineral described by Brindley and Robinson, 1947 [10] which occupies an intermediate position between kaolinite and halloysite. This was previously presumed from the studies of the rates of dehydration on heating and from the differential thermal analysis.

(*d*) *Sinai kaolins.*—The clay mineral was identified as the typical fireclay mineral, together with natroalunite in the sample containing alunite. It is of interest to note that alunite has been reported by

some authors to be associated with kaolinite and by others to be associated with halloysite.

Conclusion and discussion.

Although this investigation began with the object of identifying the clay mineral component in certain Egyptian clays, the final results are of wider interest. X-ray data, thermal analysis data, and dehydration data agree in showing that the principal clay mineral in a number of these clays is intermediate in character between kaolinite and metahalloysite, and in fact it shows all the characteristics of the type of clay mineral recently discussed by Brindley and Robinson, 1947, and by Grimshaw, Heaton, and Roberts, 1945. Since the recognition of this intermediate type of kaolin clay is quite recent, it will be useful in the first place to consider what light the present results throw on this fireclay type mineral.

The X-ray photographs fully agree with those of Brindley and Robinson, 1947, and the thermal data confirm those of Grimshaw, Heaton, and Roberts, 1945. The dehydration data, however, add to our knowledge of this mineral in that they show that the fireclay type contains combined water which is lost at the low temperatures up to 300° C.

Brindley and Robinson, 1946 [11] have already suggested that most natural metahalloysites still contain residual inclusions of water. The similarity of the fireclay mineral to metahalloysite in this respect therefore suggests that there may also be some water inclusions, though perhaps fewer, in the fireclay mineral. However, although from chemical analyses water was noticed in excess of the $2H_2O$, yet such an excess has always been interpreted as hygroscopic moisture due to the fact that the clay is not of high purity.

However, it is worth noting that the fireclay mineral occurs in transported clays in Egypt. It may be that during transportation of kaolinite, water enters between the kaolinite blocks causing a displacement and giving rise to the fireclay type mineral.

It may be that these fireclay type minerals form a series in thermal behaviour, ranging from the poor kaolinite type fireclay mineral to a typical fireclay mineral.

Finally, as regards identification and elucidation of the character of the fireclay minerals, it is considered that a combination of X-ray data, differential thermal analysis data, and differential dehydration analysis is preferable, although each separately is sufficient to identify the fireclay mineral.

Acknowledgements. –While the major part of this work was carried out at the Imperial College, a part was undertaken at the University of Leeds. The authors wish to express their grateful thanks for facilities placed at their disposal for X-ray work by Dr. G. W. Brindley and for his friendly supervision and discussion of the X-ray results. They also desire to thank Professor A. L. Roberts and Dr. R. W. Grimshaw for equally generous facilities and guidance in carrying out the differential thermal analysis.

The authors also take pleasure in acknowledging the interest shown in the progress of this work by Professor Sir Alfred Egerton and the help given in cationic exchange measurements by Mr. A. G. Pollard.

They wish to thank the Egyptian Government for the opportunity and facilities offered to one of us (G. M. G.) to carry out this work.

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2. Grimshaw (R. W.), Westerman (A.), and Roberts (A. L.), 1948. Thermal effects accompanying the inversion of silica. Trans. Brit. Ceramic Soc., vol. 47, pp. 269–279.
3. Grim (R. E.), 1939. Relation of composition to properties of clay. Journ. Amer. Ceramic Soc., vol. 22, pp. 141–151.
4. Hendricks (S. B.), 1945. Base exchange of crystalline silicates. Journ. Ind. Eng. Chem., vol. 37, pp. 625 630.
5. Bray (R. H.) and Willhite (F. M.), 1929. Determination of total replaceable bases in soils. Ind. Eng. Chem. (Anal.) vol. 1, p. 144.
6. Schollenberger (C. J.) and Dreibelbis (F. R.), 1930. Analytical methods in base exchange investigations on soils. Soil Sci., vol. 30, pp. 161–173.
7. Ross (C. S.) and Kerr (P. F.), 1934. Halloysite and allophane. Prof. Paper U.S. Geol. Surv. 185-G, pp. 135–148. [M.A. **6**–136.]
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9. Brindley (G. W.) and Robinson (K.), 1946. The structure of kaolinite. Min. Mag., vol. 27, pp. 242–253.
10. Brindley (G. W.) and Robinson (K.), 1947. X-ray study of some kaolinite fireclays. Trans. Brit. Ceramic Soc., vol. 46, pp. 49–62. [M.A. **10**–367.]
11. Brindley (G. W.) and Robinson (K.), 1946. Randomness in the structure of kaolinitic clay minerals. Trans. Faraday Soc., vol. 42-B, pp. 198–205.

Alteration of the properties of bentonite by reaction with amines.

By John W. Jordan,

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[Read August 27, 1948, at the meeting of the Clay Minerals Group at the International Geological Congress, London.]

Introduction.

THE affinity between certain organic compounds and clays has been known for many years. Lloyd[1] reported the adsorptive capacity of fuller's earth for alkaloids in 1916 without theorizing extensively about the mechanism. Smith[2] reacted organic bases and their salts with bentonite and presented evidence that the reaction was one of base-exchange or metathesis, while Hauser[3] has discovered that certain organic compounds of bentonite have the property of swelling and dispersing in organic liquids. This paper reports observations on the rather striking conversion of bentonite from the hydrophilic to the organophilic condition and proposes a mechanism to explain the observed phenomena.

Materials and methods.

The clay used in this work was a highly swelling sodium-bentonite from the National Lead Company property at Clay Spur, Wyoming. Thermal and petrographic analyses along with X-ray diffraction indicated the clay fraction of this material to consist essentially of the clay mineral montmorillonite. Base-exchange capacity of the purified dried clay mineral was found to be 100 me./100 g. as determined by the ammonium acetate method.[4] Sodium ion comprised approximately 86 % of the exchangeable bases.

In the preparation of the organic complexes the bentonite was

[1] J. U. Lloyd, Discovery of the alkaloidal affinities of hydrous aluminum silicate. Journ. Amer. Pharm. Assoc., 1916, vol. 5, pp. 381–390, 490–495.

[2] C. R. Smith, Base exchange reactions of bentonite and salts of organic bases. Journ. Amer. Chem. Soc., 1934, vol. 56, pp. 1561–1563.

[3] E. A. Hauser, Private communication.

[4] R. P. Graham and J. D. Sullivan, Critical study of methods of determining exchangeable bases in clays. Journ. Amer. Ceram. Soc., 1938, vol. 21, pp. 176–183.

dispersed at about 2 % concentration in water, the dispersion set aside to permit sedimentation of non-clay impurities, and the supernatant liquid then decanted. An aqueous solution of an organic ammonium salt was then added to the clay dispersion, ordinarily in such quantity as to provide 100 milliequivalents of organic cation per 100 grams of clay. The flocculent precipitate was filtered, washed twice by repulping, dried at about 65° C., and pulverized.

Evaluation of the organophilic character of a complex so prepared was carried out by the addition of a 2-gram sample of the powder to an organic liquid contained in a graduated cylinder. After 24 hours, the volume of the swollen solids in the cylinder was recorded. Solvation took place very slowly in many liquids, and it was found necessary to add the samples in small increments, allowing each portion to solvate and sink before adding subsequent portions.

Results and discussion.

Dodecyl- and octadecylammonium bentonite complexes were prepared for which the ratio of organic salt added to clay was varied between wide limits. It was noted that filtration characteristics were best in each case when the ratio of amine to clay was in the range of 100 150 milliequivalents per 100 grams. Retention of amine, as determined by Kjeldahl analysis for nitrogen, indicated practically complete retention of the dodecylamine up to 100 me./100 g. and relatively poor retention with further additions; retention of octadecylamine decreased continuously but gradually as indicated in fig. 1. These findings parallel Grim's observation that the larger aliphatic ammonium compounds are progressively more readily adsorbed, as the size of the compound increases, after saturation of the base-exchange capacity of the clay.[1]

The viscosity of the octadecylammonium bentonite slurry, as measured with a Stormer viscosimeter at 600 r.p.m., was found to reach a maximum near the region of complete cation exchange, corresponding to the condition of maximum flocculation of the micelles, as plotted in fig. 2. This observation, along with filtration behaviour mentioned in the previous paragraph, suggests a minimum in hydrophilic characteristics of these complexes at approximately the point of complete base saturation of the exchange capacity with the organic cations.

[1] R. E. Grim, W. H. Allaway, and F. L. Cuthbert, Reactions of different clay minerals with some organic cations. Journ. Amer. Ceram. Soc., 1947, vol. 30, pp. 137–142.

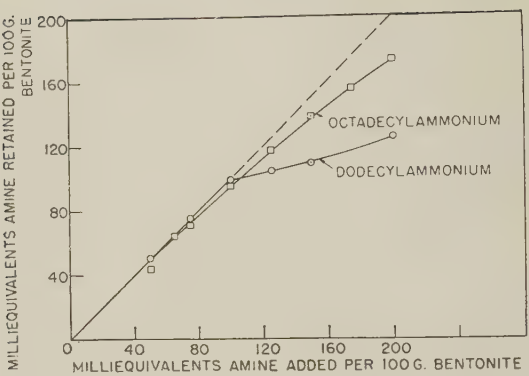

Fig. 1. Retention of organic cations by bentonite.

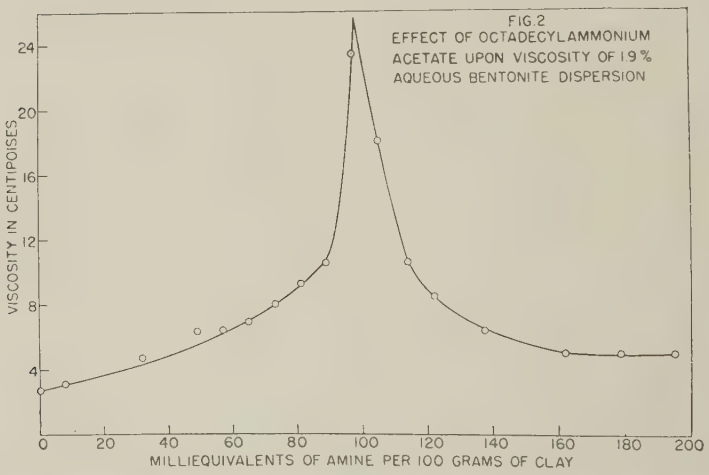

Fig. 2. Effect of octadecylammonium acetate upon viscosity of 1·9 % aqueous bentonite dispersion.

Differential thermal curves[1, 2] obtained for the untreated bentonite and for the butyl-, dodecyl- and octadecylammonium complexes after exposure to an atmosphere of 75 % relative humidity for four days point to a progressive decrease in the ability of the bentonite to adsorb moisture

[1] J. Orcel and S. Caillère, L'Analyse thermique différentielle des argiles à montmorillonite (bentonites). Compt. Rend. Acad. Sci. Paris, 1933, vol. 197, pp. 774–777. [M.A. **6**-135.]

[2] R. E. Grim and W. F. Bradley, Investigation of the effect of heat on the clay minerals illite and montmorillonite. Journ. Amer. Ceram. Soc., 1940, vol. 23, pp. 242–248. [M.A. **8**–295.]

as the size of the aliphatic chain increases. This may be readily noted in fig. 3 as a diminution in size of the characteristic endothermic peak for adsorbed water with an increase in size of the organic cation. Gieseking[1] and Hendricks[2] present a picture with which this is entirely in accord. According to them the organic molecules attached to montmorillonite through base-exchange tend to be attracted more or less in their entirety on to the surface of the mineral plates, the non-cationic portion being held by adsorptive forces. Larger molecules would obviously, therefore, reduce the water-holding capacity of the clay surface.

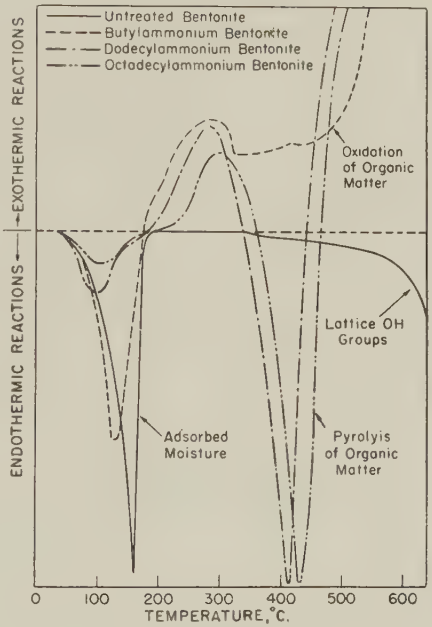

Fig. 3. Differential thermal curves.

Following the series of homologous normal primary aliphatic amines, bentonite complexes of increasingly hydrophobic character were prepared, starting with propyl- and concluding with octadecylamine. Basal-plane spacings were determined for these materials from traces obtained with a Geiger counter X-ray spectrometer. Calculating the average clay surface area per base-exchange position as 165 Å.[2] for a clay with an exchange capacity of 100 me./100 g., the basal-plane spacings have been plotted in fig. 4 as a function of amine chain length. The stepwise separation of the flakes in increments of 4 Å., the van der Waals's thickness of a methyl group, indicates that the chains lie flat along the clay flake surfaces with the planes of the zigzag chains parallel with the planes of the mineral. On

[1] J. E. Gieseking, The mechanism of cation exchange in the montmorillonite-beidellite-nontronite type of clay minerals. Soil Sci., 1939, vol. 47, pp. 1–13. [M.A. **8**–81.]

[2] S. B. Hendricks, Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals's forces. Journ Physical Chem., 1941, vol. 45, pp. 65–81. [M.A. **8**–295.]

this basis the areas covered by the amine chains have been computed from atomic dimensions[1] and included on the same graph (fig. 4). Observations appear to correlate well with theory when it is postulated that, in the case where the organic chains occupy no more than half of the available area, the organic molecules on the top surface of one lamina may fit into the gaps between those on the bottom surface of the lamina directly above it, so that the resulting separation of the two

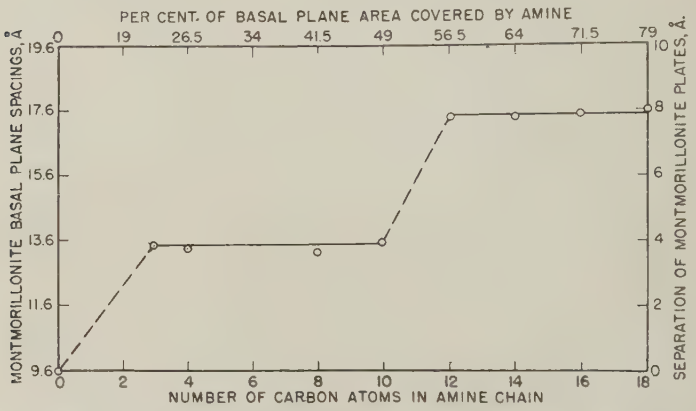

FIG. 4. Effect of amine chain length on montmorillonite basal-plane spacings.

laminae is only the thickness of one hydrocarbon chain, or 4 Å. Where the chains are longer and occupy more than 50 % of the surface area, it is obvious that adjacent flakes will be unable to approach more closely than the 8 Å. thickness of two hydrocarbon chains.

The swelling of these various complexes in nitrobenzene and in a mixture of 90 % toluene and 10 % methanol, as plotted in fig. 5, is practically negligible until a carbon chain length of 10 atoms is reached. This coincides with the point at which 50 % coverage of the clay mineral surfaces occurs and also with the qualitative observation of thorough flocculation and rapid filtration of the aqueous amine-bentonite complex. For optimum swelling a chain length of 12 or more carbon atoms and a surface coating of more than 50 % appear to be necessary.

Choosing the dodecylammonium bentonite complex as typical of the highly swelling materials, gel volumes were determined in various single organic liquids.

[1] L. C. Pauling, The nature of the chemical bond and the structure of molecules and crystals. Cornell Univ. Press, 1940.

Qualitative observation indicated that the most effective liquids were those which combined highly polar with highly organic characteristics, such as nitrobenzene, ethyl ether, diethyl ketone, and the like. This

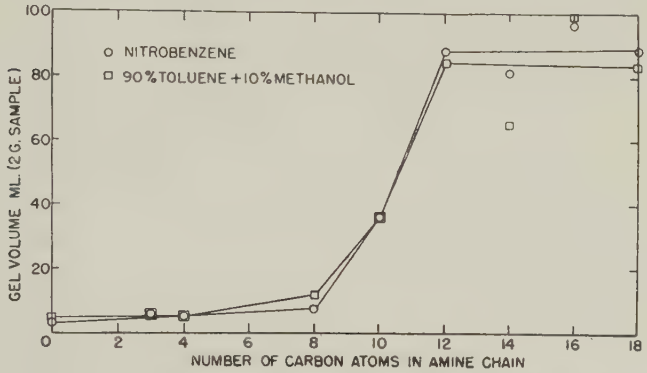

FIG. 5. Effect of amine chain length on swelling of organic ammonium bentonites in organic liquids.

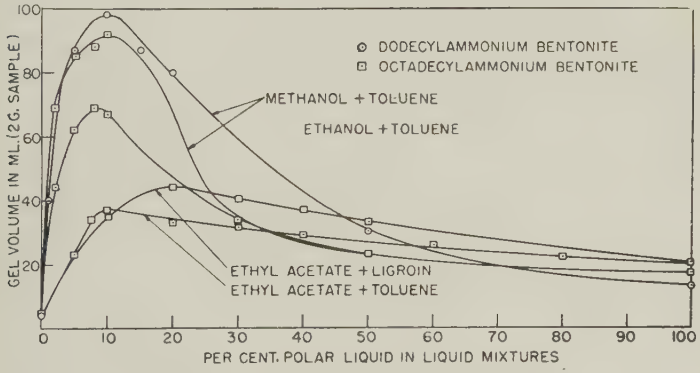
DODECYLAMMONIUM BENTONITE
OCTADECYLAMMONIUM BENTONITE
METHANOL + TOLUENE
ETHANOL + TOLUENE
ETHYL ACETATE + LIGROIN
ETHYL ACETATE + TOLUENE
GEL VOLUME IN ML. (2 G. SAMPLE)
PER CENT. POLAR LIQUID IN LIQUID MIXTURES

FIG. 6. Swelling of amine bentonites in binary liquid mixtures.

observation is borne out by the effect of binary liquid systems comprising a non-polar organic type of component in mixture with a highly polar liquid which may be of much less organic character. For example, dodecylammonium bentonite, which swells only slightly in toluene or in methanol, solvates very markedly in a mixture of 10 % methanol and 90 % toluene (fig. 6). Similarly, octadecylammonium bentonite swells to large volumes in mixtures of ethyl acetate with toluene or with ligroin.

The swelling of dodecyl- and octadecylammonium bentonites was determined in nitrobenzene as a function of the ratio of amine to clay in the complex (fig. 7). In correlation with previous observations of hydrophilic minima in the region of complete base-exchange, there was observed a maximum of swelling in organic liquids in the same region for both complexes. The extent of the swelling of these materials in nitrobenzene is surprising in consideration of the fact that the untreated clay swells to only about 30 ml. in water by the same test method.

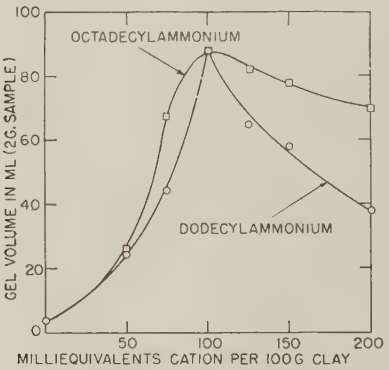

FIG. 7. Effect of varying ratio of cation to bentonite upon gel volume in nitrobenzene.

In elaborating upon the mechanism of solvation in organic liquids reference to figs. 6 and 7 should be helpful. Following the curves in fig. 7 the steep slopes of the left-hand portions of the curves indicate that satisfaction of the base-exchange capacity of the clay is essential for optimum solvation of the complex in nitrobenzene. This is probably of importance in that in an organic liquid system of this type it is desirable to mask completely or eliminate the ionic nature of the original clay by converting the sodium salt to its corresponding organic ammonium salt. The fact that further addition of organic ammonium salt beyond this point brings about a diminution in swelling may be related to a saturation of the residual adsorptive capacity of the clay by such excess reagent, thereby reducing the attractive forces available for the solvating liquid.

The part played by adsorptive forces seems well illustrated in fig. 6 where the left-hand slopes of the curves are very steep, i.e. small increments of polar liquid are extremely effective in promoting solvation of the bentonite complex. It is postulated that in a binary liquid mixture of this sort, the polar component is adsorbed on to the uncoated portion of the clay flakes. This action should tend not only to effect a further separation of the plates, making the coated surfaces more readily available for solvation, but should also completely coat the surfaces with organic matter. The completely coated flakes are therefore rendered more compatible with the surrounding liquid phase. In

somewhat different terms it is hypothesized that an association complex is formed between organic ammonium bentonite and polar liquid molecules and that this complex is then solvated by the non-polar constituent of the liquid system. Excess polar liquid beyond that required to form the association complex merely tends to dilute the non-polar component, and the degree of swelling diminishes. The above picture may be carried over to single liquid systems in which the degree of swelling may depend upon the ability of the liquid to form an adsorption or association complex and subsequently upon the compatibility of the resulting complex with the liquid, keeping in mind that the character of the complex will be influenced to an appreciable extent by the long alkyl amine chains. Thus glycerol may be strongly adsorbed, but the resulting complex could not be expected to be highly compatible with glycerol; whereas, nitrobenzene should have a strong affinity for the amine bentonite salt by reason of the nitro group and should further be quite compatible with all portions of the surface coating. Hydrocarbons alone, however, are probably only weakly adsorbed and not particularly compatible with the semi-polar complex.

Summary.—Amine-bentonite complexes have been prepared and a study made of alteration of the affinities of the bentonite in connexion with various liquid systems. Several techniques have been employed in observing the change in the clay from its naturally occurring condition to one in which it is compatible with organic liquids. A mechanism is proposed to account for the pronounced modification of characteristics.

Transformation of minerals of the montmorillonite family into 10 Å. micas.[1]

By Miss S. Caillère and S. Hénin.

Muséum National d'Histoire Naturelle, Paris.
Laboratoire des Sols, Versailles.

IN his work on the mineralogy of soils colloids G. Nagelschmidt,[2] suggests the possibility of a reversible change of the type

montmorillonite ⇋ illite ⇋ muscovite.

We have attempted to establish experimentally the existence of this transformation following fixation or departure of the potassium from between the fundamental structural sheets of the mica type. The initial material was montmorillonite from Camp Bertaux, Morocco, separated from its impurities by sedimentation. As it was evident *a priori* that the alteration of montmorillonite into illite necessitates (1) saturation of the base-exchange capacity of the minerals by potassium, and (2) the departure of the layers of water from between the structural sheets of the montmorillonite, we finally, after several attempts, were led to make use of the following technique.

The sample of montmorillonite was first of all saturated with potassium by treatment with a normal solution of KCl; then, after decantation of the excess of the solution, 200 c.c. of normal KOH solution were added per 4 grams clay. It was boiled 8 hours and, in order to avoid loss of material by projection, it was convenient to place the suspension in an Erlenmeyer flask attached to a vertical cooling column. The product was then filtered, washed, and dried for one hour in an oven. After this treatment the clay already showed a sandy consistency.

[1] Read August 27, 1948, at the meeting of the Clay Minerals Group at the International Geological Congress, London, under the title: S. Hénin, Transformation des minéraux de la famille des montmorillonites en phyllites à 10 Å. (Internat. Geol. Congr., Volume of Titles and Abstracts, 1948, p. 128). A portion of the paper had appeared as a preliminary note: S. Caillère, S. Hénin, and S. Mériaux, Transformation expérimentale d'une montmorillonite en une phyllite à 10 Å type illite. Compt. Rend. Acad. Sci. Paris, 1948, vol. 226, pp. 680–681. [M.A. **10**–368.] Translated by Dr. D. M. C. MacEwan.

[2] G. Nagelschmidt, The mineralogy of soil colloids. Techn. Commun. Imp. Bur. Soil Sci. Harpenden, 1944, no. 42. [M.A. **9**–76.]

Nevertheless it was necessary to repeat the operation three and four times to obtain a substance which, when examined with X-rays in the air, gave a diagram showing the following characteristics.

The principal spacing is 10·2 Å. and its intensity is weak in comparison with the other lines of the diagram. A third-order line at 3·2 Å. is also observed, which has essentially the same intensity as the corresponding line of illite. If one makes a diagram of the same substance, but this time immersed in the mixture of water and glycerol, no change is observed. We have, therefore, a stable mineral with 10 Å. spacing showing the characteristics of illite.

However, on treating this product for three days with a mixture of 2N-$CaCl_2$ and 10 c.c. N/10-HCl a product is obtained which on air drying shows a principal spacing of 11·7 Å. in the form of a rather diffuse ring. On the other hand, a diagram of this substance steeping in the water-glycerol mixture does not show any large spacing line, or at the most it is possible to make out a circular veil corresponding to all possible spacings between 10 and 17 Å. This series of results allows the conclusion to be drawn that the treatment we used blocks the expansion of the montmorillonite and leads to a product with properties similar to illite. The partial reversibility of the change produced by treatment with calcium salts shows, however, that this result is incompletely attained. We shall return to this subject later.

We have also tried treatment with potassium carbonate, potassium chloride, potash of several concentrations, ammonia, and soda; but only the treatment just described leads to a fairly constant result. We have never obtained it with other cations than potassium, and only when the latter was in the form of KOH of different concentrations; although with more concentrated solutions, for example 5N, the result is much less certain and the time of treatment must be reduced in order to avoid dissolving too great a quantity of the initial mineral. We may note further that on making an X-ray diagram in air of the sodium product prepared by boiling in N-NaOH it shows a principal spacing of 12 Å. and its higher orders.

We have also applied the treatment to a nontronite from Behenjy, Madagascar, and the result was essentially the same as that given by the montmorillonite. However, the nontronite thus treated is a little less stable than the montmorillonite, for it is found that the ring corresponding to the principal spacing although remaining at about 10 Å. becomes slightly diffuse on making a diagram of the water-saturated substance. It is, nevertheless, true that the behaviour

established by these experiments seems to hold for the different members of the montmorillonite family.

Verification by thermal methods.

With a view to supporting the results of the X-ray study by other observations, we carried out weight-loss analyses and differential thermal analyses on the initial and treated materials and on bravaisite.

The curves given by the Chevenard thermo-balance, which allows of a continuous recording of the weight of the substance as a function

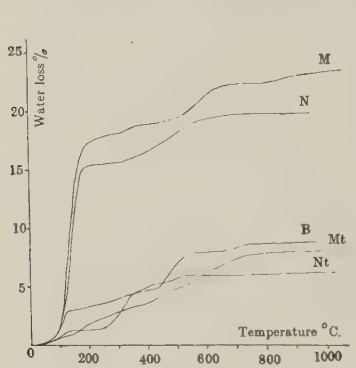

FIG. 1. Dehydration curves.

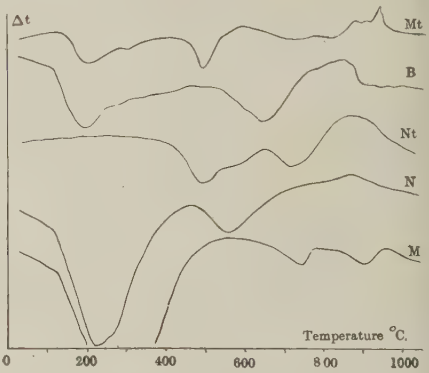

FIG. 2. Differential thermal curves.

Montmorillonite (M), treated montmorillonite (Mt), nontronite (N), treated nontronite (Nt), bravaisite (B).

of the temperature to which it is subjected, are reproduced in fig. 1. The initial samples (curve M, montmorillonite, and N, nontronite) are characterized by a loss of hygroscopic water of the order of 15 %, plus a more or less continuous loss of water of constitution, beginning a little below 300° for nontronite, and a little below 500° for montmorillonite. The bravaisite, on the contrary, shows a small loss of hygroscopic moisture, of the order of 3 %, and the loss of water of constitution shows up around 430°.

The curves corresponding to the treated montmorillonite, Mt, and the treated nontronite, Nt, show a very small loss of hygroscopic water, in accordance with the observed blocking of the structural sheets. The small water loss found with bravaisite is probably due to this mineral being a mixture of a 10 Å. material with a small quantity of 14 Å. material. As regards the loss of water of constitution, it essentially reproduces that of the initial minerals, but with somewhat lower

temperatures, and a more spread-out appearance. Apart from this last characteristic, the curves are obviously similar to the bravaisite one.

The differential thermal analysis, carried out with the Saladin–Le Chatelier apparatus, gave the curves reproduced in fig. 2, the same symbols as before being used. The montmorillonite curve (M) shows three characteristic peaks at 230°, 730°, and 900°. The nontronite curve (N) has two peaks, one at 210°, the other around 550°; finally the bravaisite curve (B) is distinguished by three peaks, one around 200°, much weaker than on the preceding diagrams, a second around 630°, relatively large but rather spread out, and lastly a rounded exothermic peak at 840°.

The treated montmorillonite (Mt) shows a weak endothermic peak at 200°, then a well-marked peak around 490° and finally a flattened exothermic feature around 920°. The treated nontronite (Nt) gives a similar curve but the second endothermic peak is around 500°, further two rounded features around 650° and 850° seem to be due to exothermic phenomena, the latter one corresponding to that of bravasite. Thus, thermal study leads to identical conclusions to those which emerged from the X-ray examination. Finally, we may note that chemical analysis of the treated montmorillonite brings out a potassium content of the order of 5 %, corresponding to that of illite.

Alteration of vermiculite.

In an attempt to further extend the preceding results, we experimented on vermiculite from Corundum Hill, North Carolina. Since this mineral occurs as platelets with dimensions of the order of a centimetre, we thought it would be necessary to reduce it to smaller dimensions. The original platelets were filed, and the resulting product sieved with a no. 100 sieve. Five grams of this powder were put into a porcelain pot with 500 grams of steel ball-bearings, and a sufficient quantity of water to form a paste. The pot was put on to an end-over-end shaker, which was operated for 30 hours. The distance covered in the interior of the pot was of the order of 20 kilometres. The bigger part of the product forms a stable suspension in water, and it may be assumed that the particles had a diameter smaller than 2 μ. The product was then purified to remove the iron introduced by the grinding, by boiling for $\frac{1}{2}$ hour in N/4-H_2SO_4.

The X-ray diagram obtained with this product did not differ essentially from the type vermiculite diagram. The procedure already described was applied to this substance. The results are not so clear as for the

montmorillonite, but an identical alteration is shown, characterized by a broadening and weakening of the central ring, which became much hazier. Its mean spacing is of the order of 11 Å. Although this result is not so conclusive as one could have wished, it still remains very probable that here also we have obtained a closing-up of some of the structural sheets. We may recall that J. W. Gruner[1] succeeded in obtaining such a closing-up with vermiculite by a combined treatment with hydrogen peroxide and ammonia; but that he did not obtain this result using other cations, in particular potassium, except by heating to 300°.

We have mentioned this last experiment, firstly, because it shows the generality of the alteration observed, and secondly, because it was carried out starting with a well-crystallized mineral. This proves that it is possible to study in the laboratory alterations which can go on in nature, and to make an experimental approach by mechanical and chemical alteration to the formative processes of sedimentary rocks.

In the present state of our experiments it is still difficult to understand the mechanism of the changes just described. Clearly, by bringing potassium ions in between the montmorillonite sheets, there is a tendency to approach the mica structure, but this fact alone does not explain why simple saturation in the cold, following by oven-drying does not bring about the same result. Moreover, if one supposes an alteration of the mineral, and the blocking of the structural sheets by decomposition products, it is not clear why ammonia or soda treatment does not lead to a similar closing-up of the montmorillonite.

We may note also that the quantity of potassium introduced is of the order of the base-exchange capacity, so the alteration can also not be interpreted by a raising of the number of potassium ions fixed; only a more thorough study of these phenomena can clarify the subject.

An attempt to transform mica into montmorillonite.

It may be taken as very probable that mica, by natural weathering, gives products similar to montmorillonite; moreover, we have seen that montmorillonite which has been transformed into mica can open up as a result of chemical treatment. We therefore attempted to bring about this change experimentally, starting either from sheet mica or from illite.

The two micas used, phlogopite and illite, were crushed following the technique described for the vermiculite study. The crushed samples were brought into the colloidal state. All the samples, illite and mica, were first treated by a solution of $CaCl_2$ and hydrochloric acid as for

[1] J. W. Gruner, Amer. Min., 1939, vol. 24, p. 428. [M.A. 7–479.]

the montmorillonite. Despite the fact that the treatments were lengthened and carried out both hot and cold, or alternated with alkaline treatment, we never obtained results indicating any opening-up of these minerals. We then used vigorous reagents, either 50 % HCl in the cold for 3 days, or hot H_2SO_4 during a variable time, from $\frac{1}{2}$ to 4 hours. In this last case, a certain amount of magnesium sulphate was added to the solution to try to fix some divalent ions between the structural sheets.

The results observed were as follows. The X-ray diagram of sulphuric acid-treated muscovite showed a slight modification of the central line, which tended to become hazy; also, several fine lines disappeared and the diagram approached that of illite. Study of the treated muscovite with the Chevenard balance showed a loss of hygroscopic water of the order of 3 %, which can be attributed to the penetration of water between the mica sheets. With phlogopite, the results were essentially the same, but the number of trials was much less than with muscovite.

Of the two illites used one comes from South Wales and was kindly furnished by G. Nagelschmidt and D. Hicks,[1] the other is a typical sample from Illinois. The sulphuric acid treatments gave products whose X-ray diagrams showed large-spacing lines which were less intense and hazier than for the initial samples. As a result of a series of unfortunate circumstances, the diagrams obtained were rather bad, which did not allow us to observe the higher-order lines of the (00*l*) series. The treated products, heating to 250° gave a weak but sharp central line. This tends to prove that opening-up of the mineral has occurred, heating having the effect, according to this point of view, of closing the structural sheets, which had been opened up by the treatment; however, it may be possible that the haziness found was due to an alteration product which was decomposed by heating. Thus, from this last series of experiments no very clear conclusion can be brought out.

The results justify us in hoping that it may be possible to open up the mica structure, for the changes brought about are certainly similar to those observed in the opening-up of the 'artificial illite' produced by treatment of montmorillonite. The only positive fact which emerges from these trials is that these minerals can only be opened up with difficulty. We may thus conclude that it is possible to obtain a change of montmorillonite or vermiculite into illite, permitting a study of the physico-chemistry of this alteration, and that the inverse change, of mica into montmorillonite in the laboratory, is very likely to occur also.

[1] G. Nagelschmidt and D. Hicks, Min. Mag., 1943, vol. 26, p. 297.

Experimental formation of chlorites from montmorillonite.[1]

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ONE of the problems which occupy the mineralogist as well as the geologist or pedologist is the mechanism of the formation and evolution of minerals in nature. In this general connexion we have been trying to clarify the possibility of passing from montmorillonite to chloritic minerals. Already in a previous work[2] we showed that on precipitating magnesium with ammonia in the presence of montmorillonite, a substance is obtained which shows certain of the characteristics of vermiculite and chlorite. Having thus shown the possibility of passing from one type to the other, we wished to clarify the mechanism of the change. We wanted to know what are the conditions of the transformation, and then to follow the montmorillonite from the moment when it was in equilibrium with the solution of magnesium chloride to the end of the alteration. Finally, it had to be established to what extent the product obtained resembled or differed from the standard minerals. These different points will be considered in succession.

Mechanism of the transformation.

In the original technique, a very concentrated suspension of montmorillonite, of the order of 100 grams per litre, was mixed with a 20 % solution of magnesium chloride in the proportion of 300 c.c. of suspension to 200 c.c. of the solution. After three days the clear supernatant solution was decanted, then 20 drops of NH_4OH were slowly added, with vigorous shaking. We repeated this procedure, using $MgCl_2$ solutions of concentration varying from 5 to 40 %, adding 20 to 60 drops of pure ammonia for each concentration.

[1] Read August 27, 1948, at the meeting of the Clay Minerals Group at the International Geological Congress, London, under the title: S. Caillère, Expérience sur la formation et l'évolution des chlorites et vermiculites. (Internat. Geol. Congr., Volume of Titles and Abstracts, 1948, p. 127.) Translated by Dr. D. M. C. MacEwan.

[2] S. Caillère and S. Hénin, Compt. Rend. Acad. Sci. Paris, 1947, vol. 224, p. 53.

[M.A. 10–368.]

The results of this series of trials show that, up from the 10 % concentration, using 60 drops of ammonia, a constant result, according to X-ray examination, is obtained. On the other hand, previous trials in which the ammonia treatment was applied to a Mg-montmorillonite — that is to say, one in which the base-exchange capacity was saturated with Mg, without any excess of ions in the solution—did not show the transformation. In these circumstances, one is led to conclude that an excess of Mg ions can penetrate between the structural sheets, and be precipitated there. This conception makes us suppose that the variable space between the montmorillonite sheets, which we will call Δ (after MacEwan),[1] is accessible to an excess of cations and the corresponding anions. To justify this point of view, we first observed that this space remained open even when the mineral was immersed in a relatively concentrated solution; and secondly we sought to bring out the influence of time, since the question naturally arose whether the diffusion of ions in this relatively narrow space was slow or fast.

The determination of the principal spacing of the clay in concentrated salt solution was carried out in the following manner. After the clay had been in contact for three days with solutions of strengths varying from 5 to 40 %, a small quantity of substance, for X-ray examination, was taken from the flocculate which had come down to the bottom of the vessel. Despite the high scattering power of the solution, it was possible to find out that the principal spacing remained constant at 17·6 Å. Thus it may be concluded that there is no apparent effect which would allow one to suppose a notable concentration difference between the solution in the Δ space and the external solution. Consideration of the action of the ammonia leads one to suppose that the OH ions must penetrate between the structural sheets, to allow the precipitation of magnesium hydroxide there. This fact is rather surprising, for one might have thought that the anions would find it difficult to penetrate into this space in view of the presence of negative charges carried by the montmorillonite sheets.

However, this conception is supported by the results of F. Kayser and J. M. Moch,[2] who were able to precipitate silver chloride in the Δ space by treating a Ag-montmorillonite with sodium chloride. This experiment proves even more conclusively than the one just described the possibility of an anion penetrating between the structural sheets; for the existence of hydrolysis phenomena could be explained by the

[1] D. M. C. MacEwan, Trans. Faraday Soc., 1948, vol. 44, p. 349.

[2] F. Kayser and J. M. Moch, Compt. Rend. Acad. Sci. Paris, 1948, vol. 226, p. 251.

presence of OH ions in the Δ space, without supposing that they come from the external medium. Such is clearly not the case in the formation of sodium chloride. We may thus conclude that substances can be precipitated in the Δ space.

To decide with what speed the magnesium chloride penetrates between the structural sheets, we precipitated the hydroxide after different times of contact of the clay with the solution. X-ray examination of the altered products did not allow any influence of time to be brought out, the product obtained after 5 minutes' contact, and after 3 days, giving essentially the same diagram. It follows that the penetration of the excess of salt must be very rapid if not almost instantaneous.

Let us consider now the mechanism of formation of the hydroxide layer. Initially, we have a Mg-montmorillonite and a solution of magnesium chloride. Adding ammonia, we get:

$$\text{Mg-montmorillonite} + MgCl_2 + 2NH_4OH = NH_4\text{-montmorillonite} + Mg(OH)_2 + 2NH_4Cl.$$

If an X-ray examination is made of the gel in equilibrium with the $MgCl_2$ solution before precipitation, the mineral shows a spacing of 17·6 Å. as already mentioned. A diagram taken immediately after the precipitation, without modification of the humidity of the medium, shows an almost identical spacing as far as one can judge, the diagram being diffuse.

Thus, a brucitic layer and a water layer must exist together in the Δ space. If, now, the product is allowed to dry in the air, we find that it has a principal spacing of 15·2 Å., and shows a (00*l*) series similar to that of the oven-dried product, but with more diffuse lines. Thus the water layer remaining in the product after precipitation of the magnesium is especially labile, and the stable form is the one we obtained. Furthermore, on damping the air-dried substance and making an X-ray diagram, one finds that already it is relatively stable, with only a slight tendency to swell. Finally, after drying to 105° a spacing of 14·1 Å. with a well-defined (00*l*) series is obtained, which is stable on moistening with water.

Treatment in the cold of the substance thus obtained, with a large excess of 5 % hydrochloric acid for one hour, leads to the complete disappearance of the (00*l*) series.

These trials show that it is relatively easy, by precipitating magnesium with ammonia from a concentrated solution, to obtain a stable 14 Å. micaceous product, whose X-ray diagram resembles that of a chlorite. We will now examine how far one can identify the two substances.

Comparative study of the artificial product and of the similar minerals montmorillonite, vermiculite, chlorite.

So far, the transformations have been followed only with X-rays. We will thus begin by comparing the diagrams of these different minerals.

Montmorillonite.	Treated montmorillonite.	Vermiculite.*	Chlorite.†
15·3 (vs)	—	—	—
—	14 (vs)	13·7 (9)	13·7 (7)
—	7·2 (m)	—	7·04 (8)
—	—	—	5·25 (2)
4·80 (vw)	4·76 (m)	—	4·68 (9)
4·42 (s)	4·42 (vs)	4·43 (1)	—
—	—	—	3·92 (2)
—	3·60 (w)	3·55 (3)	3·51 (10)
3·12 (m)	—	3·10 (1)	3·13 (1)
—	2·94 (w)	2·85 (3)	2·83 (7)
2·80 (vvw)	—	—	—
—	—	—	2·71 (0·5)
—	—	2·63 (1)	—
—	—	—	2·58 (7)
2·56 (vs)	—	—	2·54 (5)
—	2·43 (mw)	2·38 (3)	2·43 (6)
—	—	2·19 (1)	2·25 (4)
—	2·14 (vw)	2·07 (1)	2·02 (7)
—	—	—	2·00 (6)
1·72 (m)	1·86 (w)	1·73 (0·5)	—
—	—	1·67 (3)	—
1·60 (vvw)	1·57 (w)	—	1·56 (10)
1·51 (m)	1·52 (s)	1·53 (3)	1·53 (10)

* R. C. McMurchy, Zeits. Krist., 1934, vol. 88, p. 420. [M.A. **6**–45.]
† J. W. Gruner, Amer. Min., 1934, vol. 19, p. 557. [M.A. **6**–181.]

It may be seen that the diagram of the alteration product resembles that of chlorite. The first five lines of the (00*l*) series correspond to an approximately rational series of spacings, and are near to those of chlorites. These lines are absent from the vermiculite and montmorillonite diagrams. Further, we may recall that the diagrams of the alteration products of vermiculite and of chlorite are stable in water. Thus, a close analogy may be traced between the diagram of the treated montmorillonite and of chlorite.

However, if X-ray photographs are made, in air, of the treated product and of chlorite after heating them to 400° for 24 hours, a marked difference between the two is noted. The altered montmorillonite no longer gives the (00*l*) chlorite lines, showing that the brucitic layer formed was much less stable than that of chlorite itself. This result is

in accord with the behaviour on hydrochloric acid treatment, which also pointed to the more labile nature of the magnesium hydroxide precipitated in the Δ space.

We thus cannot say that the product obtained is identical with chlorite. We have, further, already remarked in a previous work,[1] with reference to the water-loss and the result of acid attack of chlorite, that the brucitic layer must be attached by very strong chemical forces to the mica-type sheets, thus explaining in particular the fact that chlorite is decomposed only at 550° by heat, whereas gibbsite and brucite are completely dehydrated at 350° and 450° respectively. We may therefore suppose that, in the case of our product, the magnesium hydroxide is simply precipitated between the sheets.

The chemical analysis suggests an interpretation of this behaviour. The table below collects together the composition of the four dehydrated products.

	Initial montmorillonite.	Treated montmorillonite.	Vermiculite.*	Chlorite.†
SiO_2	55·4	49·8	46	35·80
Al_2O_3	36	29	23·2	23·40
CaO	2·5	2·3	—	—
MgO	6·1	18·9	30·8	41·00

* Mean composition according to J. W. Gruner, 1934. [M.A. **6**–181.]

† Composition of clinochlore from Besafotra, Madagascar, after J. Orcel, 1927. [M.A. **3**–372.]

We see that the altered product still differs quite notably in composition from clinochlore which, of all the chlorites, might come closest to our product. The magnesium deficit which emerges implies that the newly-formed brucitic layer is incomplete, and this would explain to a certain extent the behaviour of the product both on heat-treatment and on acid attack. The silica content is quite close to that of vermiculite, but there is still a magnesium deficit by comparison with this latter mineral which is rather difficult to explain. One may then conclude that from the chemical point of view the product tends to approximate to the chlorites and vermiculites without, however, being completely the same.

The comparison of the differential thermal curves obtained with the Saladin-Le Chatelier apparatus brings out the following special features. The curves of montmorillonite (M, fig. 1), of vermiculite (V), and of treated montmorillonite (Mt) all show an important endothermic feature

[1] J. Orcel, S. Caillère, and S. Hénin, Compt. Rend. Congrès Soc. Savants, Strasbourg, 1947 (in the press).

due to the loss of hygroscopic water. However, the two latter substances do not show the feature so markedly as montmorillonite, corresponding to the fact that its Δ space is larger. In the altered product, a part of this space is filled with magnesium hydroxide. Furthermore, vermiculite shows a peak at 370°, and this feature is also found, very faintly, in the treated montmorillonite. Comparing now the high-temperature peaks, the four substances are seen to have a first endothermic feature, varying

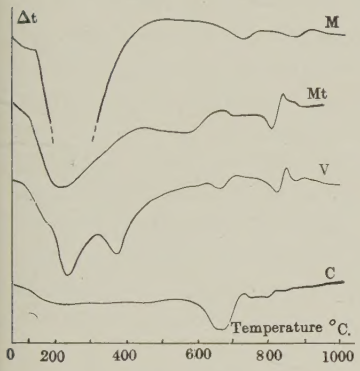

FIG. 1. Differential thermal curves.

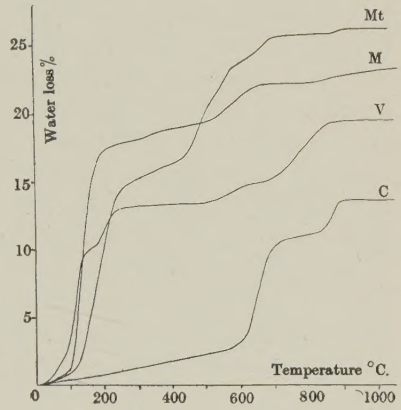

FIG. 2. Dehydration curves.

Montmorillonite (M), treated montmorillonite (Mt), vermiculite (V), chlorite (C).

from large to small in the order: clinochlore (C) large peak at 670°; treated product, fairly large peak, spread out from 570° up; montmorillonite, medium, well-developed peak at 730°; vermiculite, small peak at 660°. Further, these substances have a second more or less marked endothermic peak between 800° and 820°. Finally, the chlorite, the altered montmorillonite, and the vermiculite show two little exothermic features, the one at 650°–700°, the other about 850°–870°. The curves have other less important features, whose interpretation is difficult, but which, together with the preceding data, further reinforce the analogy of the treated product with chlorite, and (more especially) with vermiculite. Thus thermal studies confirm the conclusion which emerges from an examination of the X-ray diagrams, that the treated montmorillonite resembles the chlorites and vermiculites.

The weight-loss curves (fig. 2), recorded with the Chevenard thermobalance, show first of all a loss of hygroscopic water taking place up to about 240°, about which the same remarks may be made as for the

differential thermal analysis curves. Further, all four substances show two regions of water-loss whose relative and absolute magnitude vary from one to another. It may be noted that the curve of the treated product shows a markedly larger weight-loss than the initial montmorillonite, approaching the weight-loss of the vermiculite and the chlorite. However, this water goes off at a lower temperature from the artificial product than from the two minerals.

These results thus allow us to link up our magnesian product with chlorite and with vermiculite. Comparing the high-temperature water-loss of the initial montmorillonite and of the transformation product we see that, reckoning this water-loss from the base of the first inflexion, at 420° for the treated product and 430° for the initial montmorillonite, the first loses 9·5 % water and the second 4 %, an excess of 5·5 % water to be attributed to the water fixed as magnesium hydroxide. This amount would represent 12·2 % of MgO fixed between the structural sheets, or almost exactly the excess of magnesium shown by the chemical analysis. Without wanting to attach too much importance to this agreement, we can none the less say that the increase of water-loss at high temperatures confirms the fact that a part of the magnesium is precipitated between the sheets.

Use of different cations.

The composition of chlorites being very varied, the constituents of the brucitic layer ought also to differ considerably. Furthermore, several cations can give hydroxides with the gibbsite-brucite structure. For these two reasons, one might suppose that, applying the preceding treatment to montmorillonite in presence of solutions of cations having these characteristics, one could obtain the same sort of alteration.

Our experiments have been done with nickel, cobalt, ferrous and ferric iron, aluminium, and chromium ions. The results enable us to classify the cations into 2 groups:

(1) Those giving rise to the same modification as magnesium, such as nickel and cobalt;

(2) The others, whose behaviour is discussed below.

Treatment by cations of the first group.—Using the range of concentrations already used, the treatment leads to products whose X-ray diagrams can be classed between the following two extreme types.

With additions of ammonia of the order of 10 to 20 drops, the X-ray

diagram shows a (00*l*) series with four successive orders, the first being by far the most intense. These substances are not very stable in water, because on taking an X-ray photograph of the moist substance, an increase of the (001) spacing is found.

With a larger quantity of ammonia (80 to 100 drops) the diagram remains quite stable even when the substance is moistened. It then shows the following characteristics: the first order has almost completely gone; the second order is extremely intense; the third order is weak; but the fourth order very clear. Thus the (00*l*) series of these products appears to be complementary to that of montmorillonite, since in the latter it is the even orders which disappear.

The result can be interpreted as follows: the presence of a layer of ions of high-scattering power in the Δ space leads to the formation of two 7 Å. layers of similar scattering power. One is formed by one of the tetrahedral layers, and the octahedral layer of the montmorillonite; the other by the second tetrahedral layer of the montmorillonite and the newly-formed octahedral layer. In these conditions, when the crystals make an angle with the incident beam having a Bragg angle corresponding to 14 Å. spacing, the reflecting planes 7 Å. apart give equal reflected intensities, but in opposite phase; the reflection corresponding to the 14 Å. spacing is thus extinguished, and all the odd-order reflections are weak or absent. The even-order reflections, on the other hand, are intensified.

It might obviously be wondered if the new diagram does not indicate the existence of free hydroxides. This objection does not seem tenable for the following reasons. The nickel hydroxide obtained by precipitation with ammonia gives no 7 Å. line. Further, though the diagram of the treated product does not have the large spacing line of montmorillonite, it none the less shows (*hk*0) lines of normal intensity. It is not very probable therefore that our result could be due to a mixture of nickel hydroxide and montmorillonite. Further, like the magnesian products, these substances are not heat-stable. After heating to 400° the 7 Å. line disappears and a halo appears situated around 10 Å. This behaviour seems readily attributable to the destruction of the hydroxide layer and the formation of a 10 Å. micaceous mineral.

It is further possible to get intermediate diagrams, in which the intensity of the (00*l*) series of lines varies, from which we may conclude that the behaviour of nickel and cobalt is quite analogous to that of magnesium. This analogy deserves to be stressed, for we had already noted it in our research on the synthesis of antigorite. In the course

of this work we were able to obtain silicates of Mg, Ni, and Co at low temperatures and in similar conditions; while such preparations could not be obtained using the following group of ions.

Treatment by cations of the second group.—In contra-distinction to the facts observed in the preceding work we were never able, either with ferrous or ferric iron, chromium, or aluminium, to obtain a comparable alteration to those previously described, despite the existence of aluminous, ferriferous, and chromiferous chlorites.

After precipitation of the hydroxides by ammonia, the X-ray diagram is still very close to that of the initial montmorillonite; and furthermore the diagram of the moistened product shows an increase of the first-order spacing. The characteristics of the weight-loss curves are, however, greatly altered, which leads one to suppose that there is none the less a part of the hydroxides precipitated between the sheets. Only a more complete study of the treated montmorillonite after heating to different temperatures would enable a definite conclusion in this sense to be drawn. The special behaviour of this group of substances could be attributed to the fact that the second group cations on precipitation give rise to hydroxides with different structures from those of the first group hydrates.

Conclusion.

This work shows that, by precipitation of magnesium, nickel, and cobalt between the structural sheets of montmorillonite, substances are obtained which give X-ray diagrams similar to those of chlorite, or of certain vermiculites. The analogy between these two substances is also confirmed by thermal analysis, weight-loss diagrams, and chemical study.

Only a smaller stability on heating and on acid treatment distinguishes rather clearly this alteration product from the two minerals, chlorite and vermiculite. The analogy seems to us, however, to be good enough to warrant the consideration of this type of change as one of the possible mechanisms of alteration of montmorillonite in nature.

Finally, as a consequence of these results, it may be suggested that the vermiculites represent a type of mineral which comes close to the chlorites, but in which the brucitic layer is rudimentary.